FOODS:

THEIR COMPOSITION AND ANALYSIS.

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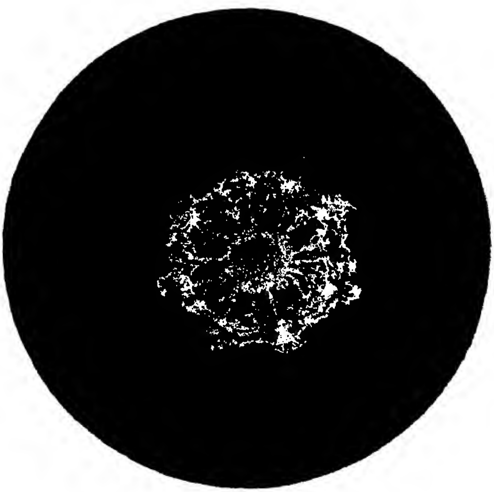

No. 2. SPERMACETI.

FOODS:

THEIR COMPOSITION AND ANALYSIS.

A MANUAL FOR THE USE OF ANALYTICAL CHEMISTS AND OTHERS.

WITH AN INTRODUCTORY ESSAY ON THE HISTORY OF ADULTERATION.

BY

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With Numerous Tables and Illustrations.

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PREFACE.

THE following pages are an instalment of the Second Edition of the Author's "*Manual of Practical Chemistry*"—the First Part of the New Edition being now issued separately under the title of "*Foods: their Composition and Analysis*," and the Second Part under that of "*Poisons: their Effects and Detection.*" The reasons for the alteration of the title are sufficiently obvious: the present appellation is distinctive, rendering impossible any confusion between this Manual and others (of a widely different scope and manner of treatment) which might come equally under the designation, "*Practical Chemistry.*"

The present Volume, however, is not a mere reprint of the Division, "*Foods*," in the First Edition. It has been thoroughly revised and re-written, where necessary, and enlarged by the addition of new matter to more than double the number of pages allotted to the subject in the original work.

The Historical Introduction prefixed is the result of considerable labour and research, and, it is hoped, will be found—together with the review of English Legislation, Past and Present, relative to Adulteration—not without interest. As in the First Edition, abstracts of a few legal cases are given at the end of the chief Articles. These have been carefully selected, as illustrative either of ingenious defence, or of certain points in the Adulteration Acts. It has often been remarked that private individuals rarely avail themselves of the "Sale of Food and Drugs" Act. This, probably, is due to insufficient acquaintance with the technical details of the mode of procedure, and the Author has, therefore, been careful to explain the "Purchase" sections fully in their relations both to the official Inspector and to the private purchaser. In the Appendix will be found the Text, entire, of the English laws at present in

operation, as well as the best and most recent of the American Acts relating to the Adulteration of Food.

In the Scientific Portion of the work, the professional Chemist will find details of most of the processes of any value in Food Analysis hitherto published, and in all cases (either by the aid of Footnotes, or in the Bibliography appended to each Article) the original source of the information is indicated. In addition, are given a large number of Processes, either invented or improved by the Author, and not previously published—such, *e.g.*, as those described in the Articles on Milk, Butter, Tea, Flour, Water, &c.

Numerous Tables, some of which are indispensable and others convenient, have also been added; and new Illustrations, from original drawings, introduced.

The Article on *Milk*—a special feature of the First Edition—is still further enlarged, and contains the Author's most recent researches on the subject. It may, perhaps, be considered a fairly complete Monograph. In the Article on *Water* (added by request) the application of an improved process for combustion in a vacuum is detailed, and the importance of Biological methods of examination is insisted upon—not as supplementary to Chemical tests, but as of equal (if not of superior) value to these.

Though the scope of the Manual is mainly that of a Laboratory Handbook, yet the dietetic and medical aspects of the more important Foods are, where necessary, fully considered, and the Author believes that a great proportion of the work is thus of that general interest which will render it useful to those who, without much chemical knowledge, yet desire to have, in a form admitting of easy reference, the latest information relative to Foods and Beverages.

In conclusion, he can only express a hope that the work, in its new shape, will be found widely useful, and more worthy of the very kind reception accorded to the First Edition.

COURT HOUSE, ST. MARYLEBONE,
April, 1882.

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ERRATA.

Page 48, line 12 from top—*For* 41 and 42 Vict., c. 30, *read* 42 and 43 Vict., c. 30.

Page 91, line 8 from bottom — *For* Erythrophylll; *read* *Erythrophyll.*

Page 99, Fig. 13—The curved end of the tube should have been indicated by the letter G.

Page 122—*For* $\frac{16}{0143 \cdot 2}$ *read* $\frac{16}{(0143)2}$

Page 172 (Bibliography)—The reference to Cleavor's paper on "Alum," should be *Pharm. Journal* [*3*], *Vol. iv., 851. 1874.*

Page 172 (Bibliography)—*For* Dupré, A., *Chem. News, read Chem. News, May, 1874.*

Page 172 (Bibliography)—The reference to Crookes' paper should be *Chem. News, 1861.*

Page 173 (Bibliography)—The reference to Young's paper should be *Analyst, April, 1877.*

Page 201, foot-note—*For* "Sinely," *read* "*Sinety.*"

Page 261—*For* $100 - \frac{100 + 2 \cdot 5}{9} s - f = x$,

$$\textit{read}\ 100 \frac{100 + 2 \cdot 5}{9} s - f = x.$$

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PART I.

HISTORY OF ADULTERATION.

FOODS: THEIR COMPOSITION AND ANALYSIS.

PART I.—HISTORY OF ADULTERATION.

I.—EARLY NOTICES OF ADULTERATION, ESPECIALLY IN ENGLAND.

§ 1. Before adulteration commences, commerce must develop. In primitive states of society, there may be knavish tricks, ignorant bartering, substitutions of bad for good, falseness and meanness of all kinds, but no systematic sophistication is possible. Again, in the semi-pastoral state (as it existed in some parts of Scotland a century ago), in which the food of a family is raised from the soil on which they dwell, and clothing produced from their own sheep and spun into textile garments at their own fireside, commercial frauds are unknown or undeveloped.

There are several notices of ancient sophistications practised by the Greek and Roman traders; but it is from the Middle Ages that the most copious and interesting materials for a history of adulteration are obtained—a page of history but little explored, yet abounding with curious facts more or less illustrative of the manners of the times.

The mixing, or, rather, alloying of gold or silver with the baser metals, may be justly considered of the nature of adulteration, and has prevailed contemporaneously with the art of coinage. The well-worn tale of the detection of the base metal in the crown of Hiero by Archimedes, some two and a half centuries before Christ, may be accepted as probably the earliest scientific detection of adulteration. The process used by the philosopher of Syracuse when discharging the duties of a *public analyst*, and now called specific gravity, is quantitative as well as qualitative, and,

though purely physical, is used daily by all engaged in practical chemistry.

Vitruvius* in his work on architecture describes the adulteration of minium with lime. He also gives a simple process for its detection: heat to redness on a sheet of iron; if pure, it will blacken, but on cooling return to its former hue.

Dioscorides alludes to the adulteration of opium with gum and with the milky juice of glaucium and lactuca. The test for distinguishing the pure from the false was primitive: the opium was to be burnt; if pure, the flame was clear and brilliant, but the adulterated burned with difficulty. The quality of the opium was also to be judged by its behaviour when exposed to the rays of the sun; when opium of good quality liquefies, it looks as if it had just come from the plant.† He also specifies the adulterations of several drugs; as, for example, the mixing of styrax resin with styrax sawdust.

Pliny, among other matters, alludes to the frauds practised by bakers; for they added to the bread a white earth, soft to the touch and sweet to the taste, which was obtained from a hill called "*Leucogee*," situated between Pouzzoles and Naples. It has been suggested that the white earth was carbonate of magnesia; this is doubtful.‡

He also speaks of the adulteration of aerugo (under which name was confounded both the acetate and sulphate of copper) with shoemaker's black *atramentu sutorium*, and gives a true chemical method for its discovery. Paper is to be soaked in the juice of galls; if the aerugo is pure, it will not turn the paper black. Another method was to put the substance on a sheet of red hot iron; if sulphate of iron had been added, it became covered with spots.§

The adulteration of wine in Athens necessitated the appointment of a special inspector, whose duty it was to detect and stop these practices. Greek history has handed down the name of one *Canthare*, who excelled in ingenious mixtures, and knew how to impart the flavours of age and maturity to new wines. His ingenuity was such, that it was commemorated in the proverb: "Artificial as Canthare."

In Rome, also, wine was much tampered with; even the rich, according to Pliny, could not obtain the natural wines of Falerno, for they were adulterated in the cellars; and certain wines from Gaul had an artificial colour given to them by means of aloes and other drugs.||

* Vitruvius, i. ix. c. 13. † Dioscorides, iv. 65; Pliny, xx. 76.
‡ Pliny, xviii. 29. § Pliny, xxxiv. || *Op. cit.*

§ 2. In our own country, and in Europe generally, from the eleventh century onwards, the bakers, the brewers, the "pepperers," and the vintners, were most frequently accused of corrupt practices. We must not, however, judge too harshly of the tradespeople of that epoch, for morality was generally low, and adulteration an innocent pastime when compared with the frequency and magnitude of midday highroad robbery and midnight violence.

In the latter part of the twelfth century, that which would now be called crime became the favourite amusement of the principal citizens, "who would sally forth by night, in bands of a hundred or more, for an attack upon the houses of their neighbours. They killed without mercy every man who came in their way, and vied with each other in brutality. . . . False weights, false measures, false pretences of all kinds were the instruments of commerce most generally in use. No buyer would trust the word of a seller, and there was hardly any class in which a man might not with reason suspect that his neighbour intended to rob or even to murder him."*

ASSIZES OF BREAD—BAKERS.

§ 3. The sale of bread was regulated in England as early as the fourth year of the reign of John, by what was called the "Assize of Bread," the original object of which was to regulate the price of bread by limiting the profit of the baker on each quarter of wheat, so that the price of the loaf should bear a certain proportion to the price of the quarter of wheat. The assize of John's reign continued in force until 1286, when it was repealed by "*The Statute of Assize.*"

There were various modifications of these assizes, and they were finally abolished in 1815. The "Assize of Bread" in its influence was probably the exact reverse of what was intended. On the one hand, the development of trade was restricted injudiciously; and, on the other, the bakers often suffered unjustly, and, therefore, had a direct inducement to recover their losses by nefarious practices. Although, at the institution of the assize, adulteration with foreign substances was not the main object of the regulations, yet, as time went on, and the sins of the bakers, both male and female,† accumulated, clauses with regard to the

* "A History of Crime." By Luke Owen Pyke.

† The bakers, as well as the brewers, were of both sexes.

adulteration of bread were inserted, and the later ones may be considered collectively as the ancient English "Sale of Food Act." The assize of 1582* contained the following :—" If there be any that by false meanes useth to sell meale: for the first time he shall be grievously punished, the second tyme he shall lose his meale: the III tyme he shall foreswere the towne and so likewyse the bakers that offende. Also, bouchers that sell mesell porke or mozen flesche: for the first time they shall be grevously amerced, for the second tyme so offendinge they shall have the judgement of the pillory, for the third tyme they shall be comytted to pryson until ransomed, and the fourth tyme they shall forswere the towne, and thus ought other transgressors to be punished as cooks, forestallers, regrators of the markets when the cookes, serve, roste, bake or any otherwyse dresse, fysche or flesche unwholesome for man's body."

The assize of 1634 had some stringent regulations with regard to musty meal :—" If there be any manner of person or persons, which shall, by any false wayes or meanes, sell any meale unto the kinge's subjects, either by mixing it deceitfully or [sell any] musty and corrupted meal, which may be to the hurte and infection of man's body, or use any false weight, or any deceitful wayes or meanes, and so deceive the subject, for the first offence he shall be grievously punished, the second he shall lose his meale, for the third offence he shall suffer the judgement of the pillory, and the fourth time he shall forswere the towne wherein he dwelleth."

These extracts give some idea of the punishments inflicted on dishonest bakers during the Middle Ages in England. First offences were often visited by corporal chastisement and exposure in the pillory (generally with a rope and a loaf round the neck); fourth, and even third, convictions were considered so heinous that it was thought better to cast the man forth from the city to earn his livelihood elsewhere.

In the curious paper entitled "A Quip for an Upstart Courtier,"† there is a powerful and quaint expostulation with the different traders:—"And for you goodman baker, you that love to be seen in the open market-place upon the pillory, the world cries out on your wiliness: you crave but one deere yeare to make your daughter a gentlewoman. You buy your corne at the best hand,

* The title runs :—"Here beginneth the boke named the assyse of bread, what it ought to weye, after the pryce of a quarter of wheat, also the assize of ale, with all manner of wood and cole, lath, bolside, and tymber, and the weight of butter and cheese. Imprynted, by Thomas Wyatt, 1582."

† The "Quip for an Upstart Courtier" was written in 1592. The original is in black letter.

and yet will not be content to make your bread weight by many ounçes. You put in yeaste and salt to make it heavie: and yet all your policie cannot make it. The poore crie out, the riche find fault, and the lord maior and the sheriffs, like honourable and worshipful maiestrates, every daie walk abroad and weigh your bread, and yet all will not serve to make you honest men. But were extremities used and the statutes put in the highest degree in practice, you would have as few eares on your heade as the collyer."*

The manner of adulteration seems to have varied.† Sometimes the bread was made altogether of "putrid and rotten materials," sometimes it was good outside and bad within, and as for the addition of alum or mineral matters, such was only detected when in considerable quantity and coarsely done. The more artful mixtures required for their detection the application of a chemical science not then possessed. The following may serve as examples of a few of the earlier instances:—

One "Alan de Lyndseye, baker, was sentenced to the pillory because he had been convicted of baking *pain demayn* that was found to be of bad dough within and good dough without, and because such falsity redounds much to the deception of the people who buy such bread."

The same baker seems a few days afterwards to have been again in trouble, for "Alan de Lyndseye, baker, and Thos. de Patimere, baker, were taken and brought before the Mayor and Aldermen, and sentenced to the pillory for selling bread made of false, putrid, and rotten materials, through which who bought bread were deceived, and might be killed."‡

A similar fraud is recorded at perhaps an earlier date (A.D. 1311), for "the bread taken from William de Somersete, baker, on the Thursday next before the Feast of St. Lawrence (Aug. 10) in the 5th year of the reign of King Edward was examined and adjudged upon. . . . . Because it was found that such bread was putrid and altogether rotten, and made of putrid wheat, so that persons eating that bread would be poisoned and choked, the Sheriff was ordered to take him and have him here on Friday next after the Feast of St. Lawrence, then to receive judgment for the same."§

* The sanitary state of the bakehouses in the fifteenth and sixteenth centuries was, as a rule, bad. According to Mr. Pyke, they appear to have been the favourite receptacle for dead bodies after a murder had been committed. "A History of Crime," by Luke Owen Pyke, M.A. Vol. I., p. 256.

† In the reign of Edward I. it was enacted at one of the "Hallmotes," that no bread should be coated with bran, or so as to be found worse when broken than it was on the outside.

‡ "Memorials of London," by H. T. Riley, pp. 120, 121. § *Op. cit.*

Mr. Pyke, in his "History of Crime,"* speaks of loaves being adulterated in the Middle Ages by lumps of iron, probably referring to the following case. "On Wednesday next after the Feast of St. Matthew the Apostle (11th of Sept., A.D. 1387), in the 11th year, Richard Porter, servant of John Gibbe, baker, of Stratforde, was brought here before Nicholas Extone, Mayor of the said city, John Hafile, and other Aldermen, and questioned for that when the same Mayor on that day went into chepe to make assay there of bread, according to the custom of the city, he, the said Robert, knowing that the bread of his master in a certain cart there was not of full weight, took a penny loaf, and in it falsely and fraudulently inserted a piece of iron weighing about 6s. 8d. (4 oz.), with intent to make the said loaf weigh more. . . . . He was sentenced to the pillory with the loaf and iron round his neck, and the cause of the punishment was proclaimed by the Sheriffs."† But the placing of a mass of metal in a loaf under the circumstances recorded is somewhat different from adulteration, for the man slipped in the iron to avoid a conviction for false weights.

BREWERS AND VINTNERS.

§ 4. *Beer.*—The fraudulent practices of the early brewers are thus detailed in the Black-letter Tract before mentioned: "And you maister brewer, that growe to be worth forty thousand pounds by selling of soden water, what subtilty have you in making your beere to spare the malt, and put in the more of the hoppe, to make your drinke, be barley never so cheape, not a whit the stronger and yet never sell a whit the more measure for money. You can when you have taken all the harte of the malt away, then clape on store of water, t'is cheape enough! and mashe out a turning of small beare, like rennish wine: in your conscience how many barrels draw you out of a quarter of malt? Fie! fie! I conceal your falsehood, least I should be too broad in setting down your faults." Not only the brewer but the retailer of the beer, was also condemned.

"Last to you Tom Tapster, that take your small cannes of beere, if you see your guests begin to be drunke, halfe smal and halfe stronge; you cannot be content to pinch with your small pottes and your ostrie faggots, but have your drugges and draw

* Vol. I., p. 237. † Riley's "Memorials of London," p. 493.

men on to villany and to bring customers to your house where you sell a joint of meat for xii. pence that cost you scarce six, and if any chance to go on the skore, you skore him when he is asleep and set up a pot a day more than he hath, to find you drinking pots with your companions. To be short, thou art a knave!"

As early as the reign of Edward the Confessor, we find it recorded in Domesday Book that in the city of Chester a knavish brewer, "*malam cerevisiam faciens, in cathedra ponebatur stercoris*"—in other words, the offender was taken round the town in the cart in which the refuse of the place had been collected, and to this degradation was often added corporal chastisement.

In many towns in the sixteenth century, we find "ale-tasters," whose duty it was to inspect the beer.

In 1529, for example, the Mayor of Guildford ordered that the brewers make a good useful ale, and that they sell none until it be tasted by the "ale-taster." These officials had to take the following oath:—"You are chosen ale-tasters of this town. You shall well and truly serve his Majesty and this town in the same office. You shall at all times try, taste and assize the beer and ale to be put to sale in this liberty, whether the same be wholesome for man's body, and present those that offend, or refuse to suffer you to assay it. You shall give your attendance at all courts, and present from time to time the offenders, and all things else belonging to your office you shall do and execute. So help you God." The ale was not only tasted, but some of it was spilt on a wooden seat, and on the wet place the taster sat, attired in leathern breeches, then common enough. If sugar had been added to the beer, the taster became so adherent, that rising was difficult; but if sugar had not been added, it was then considered that the dried extract had no adhesive property. A less coarse, but not dissimilar, method was also applied by the earlier Inspectors to test the purity of milk.

§ 5. *Wine.*—The frauds of the vintners or winesellers attracted some share of public attention in the sixteenth and seventeenth centuries, as shown by municipal records, fugitive tracts and broadsides. In August, 1553, a certain Paul Barnardo brought into the port of London some wine, and there is extant an order in council directing the Lord Mayor to find five or six vintners to rack and draw off the said pipes of wine into another vessel, and to certify what drugs or ingredients they found in the said wine or cask to sophisticate the same.* At a later date the records

* *Remembrancia*, vii. 92.

of the Common Council contain a certificate from the Lord Mayor to the lords of the council stating, that the wines of a certain "Peter Van Payne" had been drawn off in his presence, and that in eight of the pipes had been found bundles of weeds, in four others some quantities of sulphur, in another a piece of match, and in all of them a kind of gravel mixture sticking to the casks; that they were conceived to be unwholesome and of a nature similar to others formerly condemned and destroyed.* In "The Search after Claret," by Richard Ames, a thin quarto, the last leaf is occupied by the following advertisement: "If any vintner, wine-cooper, &c., between Whitechapel and Westminster Abbey, have some tuns or hogsheads of old rich unadulterated claret, and will sell it as the law directs for sixpence a quart, this is to give notice, that he shall have more customers than half his profession, and his house be as full from morning to night as a conventicle or Westminster Hall the first day of term."†

Later, the vintners became more scientific in their operations. Addison (in the *Tatler*, No. 131, 1710) alluded to a certain fraternity of chemical operators who wrought underground in holes, caverns, and dark retirements to conceal their mysteries from the eyes and observations of mankind. "These subtle philosophers are daily employed in the transmutation of liquors, and by the power of magical drugs and incantations raise under tho streets of London the choicest products of the hills and valleys of France; they squeeze Bordeaux out of the sloe, and draw Champagne from an apple."

SPICES—DRUGS.

§ 6. The London pepperers, or spicers, formed a separate guild, and were under special ordinances. The ordinance, A.D. 1316, in Norman-French, has the following regulations:—"No one of the trade or other person in his name, for him shall mix any manner of wares, that is to say, shall put old things with new, or new things with old, by reason whereof the good thing may be impaired by the old, nor yet things of one price, or of one sort, with other things of another sort; also, that no man shall dub any manner of wares, that is to say, by putting in a thing that was in another bale, and then dressing the bale up

* *Remembrancia*, viii., 12th July, 1635.

† "The Search after Claret, or a Visitation of the Vintners." A Poem in Two Cantos. 2nd Ed., London, 1697. 4to.

again in another manner than the former in which it was first bought, so as to make the ends of the bale contain better things than the remainder within the bale, by reason whereof the buyer may be deceived, and so lose his goods. Also, that no man shall moisten any manner of merchandise, such as saffron, alum, ginger, cloves, and such manner of things as may admit of being moistened; that is to say, by steeping the ginger, or turning the saffron out of the sack and then anointing it, or bathing it in water; by reason whereof any manner of weight may, or any deterioration arise to the merchandise."*

In England the trades of the druggist and the grocer were combined. Drugs and groceries were sold in the same shop, and they were under the same regulations until 1617, when the apothecaries separated themselves from the grocers. Very soon after they had become a distinct body, they began to complain of the frauds and artifices of the grocers, from whom they continued to be supplied with many drugs; and, therefore, established a dispensary for the purpose of compounding the more important preparations themselves. In 1540 the physicians were empowered to search, view, and see the apothecary-wares and stuffs, and to destroy such as they found unfit for use. In 1553 very extensive powers were conferred on the College of Physicians for this purpose. "The four censors, or any three of them, shall have authority to examine, survey or govern, correct and punish all and singular physicians and practisers in the faculty of physic, apothecaries, druggists, distillers, and sellers of waters and oils, and preparers of chemical medicines, according to the nature of his or their offences." The great power of the censors was on more than one occasion abused. In 1724, for example, they burnt the drugs of one "*Goodwin*," the drugs not having been examined, and the history of the whole affair showing that the act was merely a gratification of private spite. Goodwin petitioned Parliament, and ultimately, it is said, obtained £600 compensation.

The College of Physicians compiled the first Pharmacopœia, and published it in 1613. Subsequent editions bear the date of 1621, 1632, 1650, &c. As may be expected, the early editions contain lists of very absurd and superstitious remedies, and have no pretensions to a scientific character.†

* Riley's "Memorials of London," p. 120.

† See "Historical Sketch of the History of Pharmacy." By Jacob Bell. Lond., 1861.

II.—ADULTERATION IN FRANCE.

§ 7. In France, from very early times, the general supervision of provisions, as to purity and quality, and the inspection of weights and measures, were under the "*police des commissaires*,"* and various special statutes were enacted from time to time. Thus, an ancient statute (1292) of the Paris brewers forbade the adulteration of beer; "whoever put into beer baye, pimento or '*poix resine*' was to be fined 20 francs, and his *brassins* were to be confiscated, for such things are neither good nor loyal to put in beer, for they are bad for the head and for the body, for the healthy and the sick." A later statute, dated March 16, 1630, among various sanitary provisions, forbade the use of buckwheat, "yvtoye or other bad matters under a penalty of 40 Parisian pounds." Judges were also to examine the materials before use, in order to see that there was nothing in them impure, heated, mouldy or spoiled. If such were found, the materials were to be cast into the river.†

§ 8. *Flour and Bread.*—There were various special regulations as to flour and bread; by an *Ordonnance* of the Provost of Paris, October 11, 1382, the miller was to grind the corn without mixing it, to increase his fee, with bran, pease, beans, or anything else save that which had been given him to grind.‡ Later, by a decree, dated July 13, 1420, the bakers were forbidden to be millers, it being thought that if they ground the wheat as well as made it into bread, there would be facilities for fraudulent dealing. The punishment of bakers for false bread—whether the falseness were admixture of foreign substances, the use of damaged flour, or simply light weight—was very similar to that of English bakers, except that it partook more of the character of a religious penance. Thus, in 1525, a baker convicted of "false

* "*La police des commissaires. . . il est de leurs soins de faire punir le débit des vivres corrumpus, alterez, falsifiez, les faux poids et les faux mesures.*" *Traité de la Police de la Mare.* Tom. i. liv. i. titre xi., chap. vi.

† "*La police des commissaires visitoient les marchez, et il estoit de leurs soins d'y procurer l'abondance des vivres et des autres provisions nécessaires à la subsistance des citoyens, ils empechoient qu'il ne s'y commist aucune fraude, soit en la qualité ou au prix, soit au poids ou en la mesure, ils estoient principalement chargés de se donner tous les soins a l'égard des grains, du pain, de la viande, et du vin.*" *Loc. cit.*

‡ "*Que nul meusnier ne soit si osé ne si hardy sur quanque il se peut mefaire envers le roy, en corps, et en biens, de mesler, mettre ou fair mettre en aucune manière es farines des blez qu'ils moudront aucune mixtion ou meslee, pour rendre plus grande mouture, comme de bran, d'orge, de pois, de fèves, ou autres choses quelconques, qui ne soit du blé qui leur sera baillé.*" *Traité de la Police*, t. ij. liv. v. titre ix.

bread" was condemned by the court to be taken from the Chatelet prison to the cross before the "Eglise des Carmes," and thence to the gate of Notre Dame and to other public places in Paris, in his shirt, having the head and feet bare, with small loaves hung from his neck, and holding a large wax candle lighted, and in each of the places enumerated he was to make "*amende honorable*," and ask mercy and pardon of God, the king, and of justice for his fault.* False weights were also often punished by corporal punishment. In 1491 the case of three bakers is recorded, who, having been convicted of selling loaves "too small," were stripped and beaten with rods through the streets of Paris, and were admonished for the future to sell the three kinds of bread ordered by the law, of the weight and quality they ought to be.† In still later times, we find the practice of the courts remarkably severe. In 1699, a baker named Pasquier, was convicted of converting into bread bad and unwholesome flour. Sacks filled with good flour and others filled with bad, had been found on his premises, and it was affirmed that he had mixed the two together. He was fined 500 livres, his oven demolished, and his shop closed for six months with a placard upon it stating the crime and the punishment.‡

§ 9. *Wine.*—A curious decree of the Provost of Paris, in 1371, compelled the tavern-keepers to permit any one who purchased wine, whether to be drunk on the premises or taken away, himself to see the wine drawn from the cask. The penalty was, for neglect or disobedience to this law, four Parisian pounds, one-fourth of which went to any informer.

An *Ordonnance* of January 30, 1330, forbade the mixing of two wines together; no wine-seller was to give a false name to a wine, or to give a wrong description of its age; the penalty was confiscation of the wine and a fine. Similar edicts were promulgated in 1415, 1635, and 1672. Still the evil did not diminish, and in 1708 two hundred inspectors of wine and drinks were appointed in Paris.

The "Baillie" of Bergheim, in 1718, had condemned to a month's imprisonment one André, who had falsified his wine with some poisonous plant (probably belladonna), and his wife, who had sold the wine, to a month's imprisonment, and a fine of 130 livres. This wine caused the death of one person, and the illness of several who had partaken of it. The sentence having been annulled on the appeal of the condemned to the Superior Council of Alsace, André and his wife were ultimately ordered to be led

* *Op. cit.*, tome ii. livre v. titre xii.
† *Op. cit.*, tome ii. livre v. titre xii.
‡ *Traité de la Police*, t. i. livre iv. titre iv., p. 570.

by two sergeants for one day through the streets of Bergheim, carrying placards both before and behind, with "*frelateurs de vin*" printed thereon. They had also to pay 30 livres fine, "*pour faire prier Dieu pour le repos de l'âme du défunt,*" and the fine of 130 livres, pronounced by the first judge. The council promulgated a very severe decree directed against such practices.

It was also forbidden to adulterate wine with litharge, Indian wood, isinglass, "*raisin de bois,*" or other drugs, or mixtures capable of injuring the health of those who drank the wine, under a penalty of 500 livres and corporal punishment. Even the possession of matters likely to be used for adulteration was an offence. So late as 1710, one Denys Porcher and his wife were convicted of conveying barrels of "*vin de raisin de bois*" into Paris. They were fined 30 livres, the four barrels of wine were spilt on the pavement, and the sentence placarded in Paris and various places around.

§ 10. *Butter.*—An *Ordonnance** of the Provost of Paris, dated November 25, 1396, forbade the colouring of butter with "soucy flowers," other flowers, herbs, or drugs. Old butter, likewise, was not to be mixed with new, but the sale was to be separate, under penalty of confiscation and fine.

The ancient laws of the merchant butter-sellers and fruiterers, confirmed in 1412, reiterated the above, and also forbade the sale of butter in the same shop in which fish was sold. The retail or sale of butter by spicers, chandlers, apothecaries, and generally by all carrying on offensive trades, was made illegal. A subsequent enactment in 1519 confirmed this law.

§ 11. *Drugs.*—The drug-sellers were also under regulation, and without doubt their practices, with regard to sophistication, were quite on a par with those of other trades. Gargantua in Paris is made to visit the shops of druggists, herbalists, and apothecaries, where he "diligently considered the fruits, roots, leaves, gums, seeds, the grease and ointment of some foreign parts, as also how they did adulterate them—*i.e.*, all the said drugs."†

In the Middle Ages the French apothecaries were at first confounded and amalgamated, as in England, with the merchant spicers; but in 1777 the two trades were separated, and they formed a definite body. In the fifteenth century the shops were little more than open booths, as may be seen from a miniature in "*Le Régime des Princes,*" a manuscript of the fifteenth century, preserved in the Arsenal Library, Paris.

Philip VI., as early as 1336, issued a regulation by which no

* *Traité de la Police*, tome i. livre iv. titre ix.

† "Rabelais," cxxiv., p 53.

one could be an apothecary unless he was a born or naturalised Frenchman, and a good Catholic. According to the law, neither the spicers nor the apothecaries were permitted to employ in the preparation of their medicines, drugs, confections, conserves, oils, or syrups, any sophisticated or exhausted or corrupted drugs, under penalty of a fine of fifty livres, and the seizure and burning of the merchandise thus adulterated in front of the dwelling in which it had been found.

Charles VIII. released the apothecaries from some of the strict regulations of earlier times, and both he and his successors were the authors of many edicts relative to the apothecaries and spicers; besides which these trades were regulated by local enactments in different towns.

§ 12. *Conseils de Salubrité.*—In 1802 the "*Conseil de Salubrité*" was established in Paris. It originally consisted of only four members, and took cognisance of adulteration, epizootics, unhealthy trades, and a little later of the administration of prisons and public charities. Afterwards the *Conseil* had the direction, generally speaking, of public hygiène.

The Conseil de Salubrité of the Seine in its later development was composed of fifteen titular and six supplementary members, including also several honorary members, with others, who, by virtue of their office, were members of the committee. These were, the Dean, the Professors of Hygiène, of Legal Medicine, and of the Faculty of Medicine, a Member of the "*Conseil de Santé des Armées*," the Director of the School of Pharmacy, the General Secretary of the Préfecture of Police, the Inspector-General of the bridges and causeways, besides engineers, architects, and the chiefs of the police departments. Most of the provinces followed the example of the capital, and established "*Conseils de Salubrité*." All these boards, whether provincial or Parisian, had one essential feature in common—viz., that the medical, veterinary, and chemical professions were always represented on them. Whatever expert a town possessed, would probably have a voice, and find a seat, in the "*Conseil de Salubrité*." From these health boards, or committees, very excellent reports have emanated, and they continue at the present time to do useful work.

III.—ADULTERATION IN GERMANY.

§ 13. If we turn to the records of Germany, we find that all those who adulterated foods or drinks in the Middle Ages were punished severely, with painful and dishonouring penalties, such

as public exposure of the fraud and whipping at the gate. The earliest regulations* related more to the goodness of the work and the general quality of the goods produced, than to adulteration. Every considerable trade was a little corporation, and bad workmanship or falsity in the goods offered was an offence against the guild itself; the member was consequently expelled or punished by the officers of the guild. For example, in 1272 the two sworn masters of the bakers' guild at Berlin were held responsible for seeing that good bread was baked. The tailors of Berlin and the bakers of Basil excluded a man for ever from their respective guilds, if guilty of bad workmanship (1333). The Berlin weavers, not quite so severe, excommunicated the offender against their regulations for one year (1295). The false butcher at Augsburg (1276) was expelled from the city for a month. In Nuremberg almost everything was regularly inspected; there was a *Bäckerschau*, a "*Safranschau*," and a "*Schau*" with regard to brandy, drugs, syrup, hops, roses, tobacco, iron, meat, salt-fish, honey, leather, and many other things. It was at a "*Safranschau*" in 1444, that one Jobst Fendeker was burnt, together with his false saffron, and in the following year two men and a woman were buried alive there for the same offence.†

In all the cities of Germany there were copious regulations with regard to three things—bread, wine, and drugs.

§ 14. *Bread.*—In Nuremberg, in the fifteenth century, the baker was not allowed to mix the different kinds of corn, which must be baked separately. In Augsburg, it would appear that there were no less than six different kinds of bread.‡ The punishments for offending bakers were various. In some places the delinquent was put in a basket at the end of a long pole and ducked in a muddy pool, similar treatment to that which in England befell "the Scolds."

§ 15. *Wine.*—According to an old Augsburg chronicle, it was in 1453 that the adulterated wine of the Franks first appeared in that city; but there is abundant evidence to show that wine had been tampered with previously, and in 1390, one Ludwig von Langenhaus was sentenced to be led out of the city with his hands

* A small work, "Der Kampf gegen die Lebensmittelfälschung von Ausgang des Mittelalters zum Ende des 18. Jahrhunderts, von L. Wassermann, Mainz, 1879," contains some very interesting particulars with regard to the regulations in practice in the Middle Ages both as to General Hygiène and the Adulteration of Food.

† Henry II. of France enacted that if saffron was adulterated, the offenders should be punished by corporal chastisement, the drugs confiscated and burnt.

‡ Maurer, "Geschichte der Stadtverfassung in Deutschland." Bd. III., s. 24.

bound and a rope round his neck, because of his practices in the adulteration of wine. In 1400, two wine-sellers were branded and otherwise severely punished, and about the same period a special law was enacted forbidding the sulphuring of casks, the colouring of wine, or the addition of sugar, honey, or other sweet things. In the year 1435, says the old chronicle, "were the taverner Christian Corper and his wife put on a cask in which he had sold false wine, and then exposed in the pillory. The punishment was adjudged because they had roasted pears, and put them into new sour wine, in order to sweeten the wine. Some pears were hung round their necks like unto a Paternoster." It further appears that they narrowly escaped being burnt.

In 1451, the city of Cologne made a strong representation to the governing body at Antwerp on the prevalent adulterations of wine. At Biebrich on the Rhine, in 1482, a falsifier of wine was condemned to drink six quarts of his own wine. He died from the effects.* In the fifteenth century at Ulm, every tavern-keeper had to appear at stated times before the sheriff (*Stadtrechner*†) and swear that neither he, his wife, his children, nor any one else in his name, had mixed with the wine, woad or extract of woad, chalk, mustard seed, clay, "*Scharlachkraut*," must of apples, lead, mercury or vitriol; no water might be added, and the same wine was to be retailed as bought. The *Stadtrechner* had also to see that no sour, ropy, or otherwise bad wine was sold. In the same town an *Ordonnance* of 1499 decreed, that since adulteration was most readily practised by putting substances into the cask, no cask was henceforth to be closed up save by the sworn cooper, who, on finding anything amiss, was to give information; penalty for default, a guilder.

In the fourteenth century, Nuremberg was a great centre of the wine trade; consequently in that city there were very many regulations against adulteration of wine, but they were similar to those already mentioned. At Frankfort on the Maine, on false wine being found, the cask was placed on the knacker's cart, and a red flag displayed, with the inscription "*stummer Wein*," that is, mute or dumb wine. The jailer marched before, the rabble after, and when they came to the river they broke the cask and tumbled the stuff into the stream.‡ About the same date, wine is said to

* In some places in very early times, the regular legal penalty was capital punishment; for example, in 1269, the law of Ripen punished the seller of false honey and wax with death.

† Perhaps "Stadtrechner" might be translated "Mayor."

‡ The article for sale was sometimes merely forbidden to be sold: this was especially the case with importations from other countries. For example, at Cologne, in 1483, casks of butter imported from England, which were found

have been sophisticated with the following substances: earth, eggs, albumen, argol, mustard, salt, burnt salt, sweet milk, brandy, almond milk, wheat flour, clay, and several other things.

In the early part of the seventeenth century, a circumstance happened in Wurtemberg, which led to some stringent regulations with regard to metallic contamination of wine. A number of people having been seized with colic, paralysis, and other symptoms of poisoning by lead, it was noticed that all those attacked drank one particular species of wine only; and on investigation the epidemic was discovered to be due to the contamination of the wine by the use of metallic fastenings to the casks. The occurrence is related by Gockelius,* who styles the disease "*Weinkrankheit.*"

§ 16. *Drugs.*—Those who sold drugs, roots, spices, and the like, were strictly supervised, and in the reign of Frederick the Second of Prussia the examination of drugs was made a special calling, the inspectors being appointed by the king.

In Augsburg, Frankfort, and a few other places, the trade in medicine was taxed. By virtue of this tax the druggists and doctors enjoyed a monopoly, and medicines were forbidden to be sold by other trades.

In the seventeenth century there were committees of doctors, whose duty it was to inspect the druggists, and from the committees—as in London, so on the Continent—originated the pharmacopœias. Thus *Pharmacopœia Antwerpiensis*, 1661; *P. Utrajectina*, 1664; *P. Amstelodamensis*, 1668; *Antidotarium Bononiense*, 1674; *Regia Chemica et Galenica, Geneva*, 1684, &c.†

IV.—HISTORY OF ENGLISH LEGISLATION IN REFERENCE TO THE ADULTERATION OF FOOD.

§ 17. The first General Act in this country was the Act of 1860, previous to which date individual articles, such as tea, coffee, chicory, beer, and wine, were legislated for by special statutes, the

to contain a mixture of old and new, were not allowed to enter the market. In like manner false oil was excluded from the city.

* "Beschreibung der Weinkrankheit," 1637.

† The dukes of Saxony regulated the trade of druggist as early as 1607. J. Guillaume published *Réglements entre les médecins et les apothicaires pour la visite des drogues.* Dijon, 1605. Thomas Bartolin edited the work of *Licetti Benanci—Declaratio fraudum quae apud pharmacopeos committuntur.* Franc. 1667 and 1671, 8vo.

object of which was, for the most part, to prevent the defrauding of the revenue; the health of the purchaser, and the injury done to him, being somewhat less considered, although not lost sight of.

§ 18. *Bakers—Bread.*—An Act in the reign of George IV. was directed particularly against the use of alum. Bakers, either journeymen or masters, using alum, and convicted on their own confession or on the oath of one or two witnesses, were to forfeit a sum not exceeding £20, and not less than £5; if beyond the environs of London, a sum not exceeding £10, nor less than £3. If within London or its environs, the justices were allowed to publish the names of the offenders. The adulteration of meal or flour was punishable by a like penalty, and loaves made of any other grain than wheat were to be distinguished by a large M. The possession on his premises by a miller, baker, &c., of any ingredient adjudged to have been placed there for the purposes of adulteration, was punishable by fine.

An Act passed in 1836 (6 and 7 Will. IV., c. 37) relative to bread, may be considered as a modern development of the old "Assize of Bread." It repealed the several Acts relating to bread sold out of the city of London and the liberties thereof, and beyond the weekly bills of mortality and ten miles from the Royal Exchange, and provided other regulations for the making and sale of bread, and for preventing the adulteration of meal, flour, and bread beyond the limits aforesaid. This Act made it lawful for the bakers to make bread of "wheaten flour, barley, rye, oats, buckwheat, Indian corn, pease, beans, rice, or potatoes, or any of them, and with any common salt, pure water, eggs, milk, barm, leaven, potato or other yeast, and mixed in such proportions as they think fit, and with no other ingredient or matter whatever." They were also permitted to make the bread any weight or size they chose. The bread, however (sect. 4), was to be sold by weight, and in no other manner.

Section 3 provided that no baker or other person within the limits prescribed . . . "shall use any mixture or ingredient whatever in the making of such bread other than, and except as hereinbefore mentioned, on any account or under any colour or pretence whatsoever;" penalty not less than £5 and not more than £10. In default of payment the offender could be imprisoned for a period of not more than six months, with or without hard labour,* or unless the penalty was sooner paid, the magistrates could also publish the offender's name, and defray the expense of such publishing out of the fines.

* *In the case of Cobe v. James, 41. L. J. M. C. 19, it was held that for a* conviction under this section guilty knowledge was necessary.

By section 9 no person is to put into any corn, meal, or flour, at the time of grinding, dressing, or manufacturing any ingredient or mixture whatsoever, not being the real and genuine produce of the corn or grain; nor is flour of one sort or corn to be sold as flour of another sort. Penalty not less than £5 and not more than £20.

Sections 11 and 12 provide that bread made partially or wholly of pease, beans, or potatoes, or of any other sort of corn or grain other than wheat, is to be marked with a large Roman M, under a penalty not exceeding 10s. Justices may issue a search warrant to enter a baker's premises at reasonable hours, and search for adulterated bread or substances used for adulteration. If such substances have been found, the justices may dispose of them as they think fit. The penalty for a first offence is a fine not exceeding £10 and not less than £2; for the second offence £5, and for every subsequent offence £10. In default of payment, imprisonment for not more than six calendar months. It is also lawful for the magistrates to publish the name of the offender. The Act contains various other provisions with regard to obstructing search, offences committed by a journeyman or servant, the baking of bread on the Lord's Day, &c.

§ 19. *Beer and Porter.*—An Act, passed in 1816, 56 Geo. III., c. 58, enacted that no "brewer of, or dealer in, or retailer of beer," shall receive or have in his possession, or use or mix with any worts or beer any molasses, honey, liquorice, vitriol, quassia, cocculus indiae, grains of paradise, guinea, pepper or opium, or any article or preparation whatever for or as a substitute for malt or hops. If any person contravene this provision, the officer of the excise may seize the worts and beer, together with the casks containing the same."—Penalty £200. By the same Act, druggists who sold colouring materials or malt substitutes to brewers, were liable to a penalty of £500. An Act, 7 and 8 Geo. IV., c. 52, provided that any brewer, having in possession or in use, substitutes for malt or hops, or for darkening the colour of beer, was liable to a penalty of £200, and the ingredients, beer, worts, &c., might be seized. Later on by the 10 and 11 Vic., c. 5, brewers were allowed to make for their own use a colouring matter out of sugar.*

§ 20. *Wines.*—An old statute (51 Hen. III., st. 6) forbade the use of unwholesome wine or meat. By the statute 12 Charles II., c. 25, any adulteration of wine was made punishable, with the forfeiture of £100 if done by the wholesale merchant, and £40 if done by the vintner or retail trader. Additional regulations

* At the present time, it is not illegal to mix bitter beer with wholesome bitters other than hops.

were made by I. William and Mary. All of these Acts, it is scarcely necessary to say, are now obsolete and repealed.

§ 21. *Tea.*—An Act was passed in 1725, 11 Geo. I., c. 30, which enacted that "no dealer in tea, or manufacturer or seller thereof, or pretending to be, shall counterfeit tea, or adulterate tea, or cause or procure the same to be counterfeited or adulterated, or shall either fabricate or manufacture tea with terra japonica, or with any drug or drugs whatsoever, nor shall mix, or cause or procure to be mixed with tea any leaves other than leaves of tea, or other ingredients whatsoever, on pain of forfeiting and losing the tea so counterfeited, adulterated, altered, fabricated, manufactured, or mixed, or any other thing or things whatsoever added thereto, or mixed or used therewith, and also the sum of £100."

Six years afterwards, 1730-31, a further Act was passed [4 Geo. II., c. 14] prescribing a penalty for what is termed in the statute "sophisticating tea." It recites "that several ill-disposed persons do frequently dry, fabricate, or manufacture very great quantities of sloe leaves, liquorice leaves, and the leaves of tea that have been before used, or the leaves of other trees, shrubs, or plants in imitation of tea, and do likewise mix, colour, stain, or dye such leaves, and likewise mix tea with terra japonica, sugar, molasses, clay, logwood, and with other ingredients, and do sell and vend the same as true and real tea, to the prejudice of the health of His Majesty's subjects, the diminution of the revenue, and to the ruin of the fair trader." The penalty under this statute was £10 for every pound of tea sophisticated.

The next Act was passed in 1776, 17 Geo. III., c. 29. The preamble asserts that great quantities of sloe leaves and the leaves of the ash, elder, and other trees, shrubs, and plants, were manufactured in imitation of tea, and were then sold to dealers in tea, who, after mixing the leaves with tea, sold it as true and real tea; but as the persons who fabricated or manufactured the leaves were not dealers in tea, they were not punishable by the law then in force. The Act, therefore, rendered any person, whether a dealer or not, who fabricated leaves in imitation of tea, or who mixed tea with other ingredients, or who sold, exposed for sale, or had in his custody fabricated or mixed teas, liable on conviction to a penalty of £5 for each pound of such tea, or in default to imprisonment for not less than six months, nor more than twelve. The officers of the excise were empowered to enter under warrant any premises by day or night and seize the leaves, which, on a further warrant, were to be destroyed.

§ 22. *Coffee.*—The history of the regulations with regard to coffee and chicory is rather curious, inasmuch as coffee appears

to have been adulterated almost immediately after its introduction, and legislative interference was soon necessary.

The first Act, 5 Geo. I., c. 11, 1718, with regard to coffee, recited that "Whereas divers evil-disposed persons have at the time of, or soon after, the roasting of coffee made use of water, grease, butter, or such like materials, whereby the same is rendered unwholesome, and greatly increased in weight to the prejudice of His Majesty's revenue, the health of his subjects, and the loss of all honest and fair dealers in that commodity," and went on to enact that "any person or persons whatsoever, who shall at the roasting of any coffee, or before, or at any time afterwards, make use of water, grease, butter, or any other material whatsoever, which shall increase the weight, or damnify or prejudice the said coffee in its goodness, he, she, or they shall forfeit the sum of £20 for every such offence." This penalty was increased to £100 by a subsequent Act (12 Geo. I., c. 30) passed in the year 1724.

An Act passed in 1803 (43 Geo. III., c. 129), ordered that "If any burnt, scorched, or roasted peas, beans, or other grains, or vegetable substance or substances be used, prepared, or manufactured for the purpose of being an imitation of, or in any respect to resemble coffee or cocoa, or to serve as a substitute for coffee or cocoa, or alleged or pretended by the possessor or vendor thereof so to be, shall be made or kept for sale, or shall be found in the custody or possession of any dealer or dealers of coffee or cocoa; or any burnt, scorched, or roasted peas, beans, &c., not being coffee or cocoa, shall be called by its preparer or manufacturer, possessor, or vendor thereof, by the name of coffee, or by the name of American cocoa, or English or British cocoa, or any other name of cocoa, the same respectively shall be forfeited, and together with packages containing the same, shall or may be seized by the excise." The person convicted was to be fined £100.

A subsequent Act (3 Geo. IV., c. 53) permitted persons, not dealers in coffee, to sell roasted corn, peas, beans, or parsnips whole, but not ground, crushed, or powdered.

In 1832, grocers were allowed by the Excise to keep chicory on their premises, and in 1840 a Treasury minute, dated August 4, 1840, allowed the sale of coffee mixed with chicory, a step which no doubt opened the way to wholesale adulteration. This is evident from a meeting of those interested in the coffee trade, held at the London Tavern, on the 10th of March, 1851, in which the chairman* explained that although more of what was *called* coffee was now consumed, yet that there was a less consumption

* T. Baring, Esq., M.P.

of *genuine* coffee. "We wish," he continued, "to come to the real question, and we desire that it should be publicly understood that what is coffee be sold as coffee, and that what is not coffee, being a cheaper article, and, if you will, a more nutritious article, and as eligible for consumption, be sold to the consumer at the price at which it can be afforded." A grocer from Shoreditch having produced at the meeting a compound of burnt peas, dog-biscuit, prepared earth, and a substance "which," he said, "I shall not describe, because it is too horrid to mention," went on to affirm that several tons of the same material were in existence, and that it was used as a substitute for chicory and for snuff.*

The *Lancet* also gave details about the same time of the microscopical examination of thirty-four samples of chicory, nearly one-half of which were mixtures, the substances found being roasted beans, burnt corn, and acorns. It was under the protection of this Minute, that Messrs. Duckworth of Liverpool took out a patent for the compression of mixtures of chicory and coffee into the shape of berries. Popular writers have, as usual, made the most of this patent, and the story has been retailed with additions from one book to another as a glaring instance of wholesale fraud ; but, although the purity of the manufacturers' intentions may be open to doubt, the fact remains that they did nothing against the existing law. The patent does not appear to have been profitable, and but few of the chicory berries were put in circulation.

The subject of coffee-adulteration was not, however, permitted to escape the attention of Parliament, and petitions from planters, growers, and others interested in the sale or production of coffee increased in number. In the Commons, during the course of a long debate (April 14, 1851), Mr T. Baring stated that it could not be denied that there had been a diminution since 1847 in the consumption of coffee to the extent of six million pounds, the real cause of which was the wholesale admixture of coffee with chicory—this chicory of home growth. In 1840, at the time of the issuing of the Treasury-minute suspending the law as regarded that article, all the chicory used in the country came from abroad, and as an excisable import on which duty was paid, but since the issue of the Minute it had been cultivated largely in England.

Similar statements were made in the House of Lords (July 3, 1851), on the occasion of Lord Wharncliffe's presenting a peti-

* "Adulteration of Coffee. A verbatim report of the proceedings at a public meeting held at the London Tavern." London, 1851.

tion to that House. In the following year, under the pressure of popular feeling on the subject, the objectionable Minute was rescinded, and a new Treasury-minute, dated July 27, 1852 (which was afterwards embodied in a subsequent order of the Inland Revenue Commissioners), permitted licensed dealers in coffee to "keep and sell chicory and other vegetable substances prepared to resemble coffee, provided that they be sold unmixed with coffee, in packages sealed or otherwise secured, containing respectively not less than two ounces, and having pasted thereon a printed label with the name of the seller, the exact weight and true description of the article contained therein, and provided that no such article be kept in a loose state, or otherwise than in such packages as aforesaid, in any room entered for the storage or sale of coffee." This regulation was, without doubt, irksome both to traders and consumers, since every one who desired his coffee mixed with chicory could not buy the mixture prepared, but was obliged to purchase the coffee and chicory separately, and compound it himself. Hence, many memorials were presented praying "That the sale of a mixture of coffee and chicory be not interfered with, provided each package has legibly printed thereon words plainly indicating such mixture." In consequence of these representations this Minute was also rescinded* and a new one prepared. An order of the Commissioners of Inland Revenue, dated May 13, 1853,† followed, requiring that on every package containing a mixture the words "This is sold as a mixture of chicory and coffee," be printed in capital letters of Roman character, of at least one-eighth of an inch in height, on the outside of the packages or canisters, on the same side of which there was to be no other printing or writing. On no other part of the package, further, was there to be any other writing save the name and address of the seller.

It would be a great error to suppose that these minutes of the Treasury, and subsequent orders of the Revenue Commissioners, had for their leading object the prevention of adulteration in its reference to the health of the subject. It will at once be noticed that they only touched on "excisable articles," and it was entirely a fiscal question. In a word, had the sophistication been of such a nature as to increase instead of diminish the revenue, the Treasury would have let it pass without notice.

§ 23. *The Select Committee of 1855.*—The prelude to legislation on adulteration as a whole, was the appointment of "A Select Parliamentary Committee," which entered on its labours in 1855.

* Parl. Paper, No. 165, Vol. xcix., sess. 1852-53.
† Parl. Paper, No. 508, sess. 1854-55.

The early appointment of this committee was, without doubt, due to the influence of the late Mr. Wakley, the able and courageous editor of the *Lancet*. In 1850 Mr. Wakley had established, in connection with his powerful journal, "*The Lancet Sanitary Commission*," of which commission Dr. Hassall was the leading spirit, with Dr. Letheby as occasional coadjutor in matters purely chemical, and (what at that time was of great importance) with the assistance of a consummate artist, who drew microscopical objects with the most remarkable fidelity.

The "Analytical Sanitary Commission" was commenced in the first number of the *Lancet* for 1851, and the scope of the inquiry, as stated by the editor, was as follows: "We propose, for the public benefit, to institute an extensive and somewhat rigorous series of investigations into the present condition of the various articles of diet supplied to the inhabitants of this great metropolis and its vicinity. . . . Special features of the inquiry will be that they are all based upon actual inquiry and experiment; the microscope and the test tube will be our constant companions." Notice was also given that at the expiration of three months the names and addresses of the shopkeepers from whom purchases had been made would be given; but at the commencement the street alone was to be indicated. The promise was kept, and hazardous although the experiment most certainly was, yet in April we find the names of large firms freely published, and, so to speak, "pilloried," for having sold impure and false goods.

In 1855 Dr. Hassall collected the articles which had been published in the *Lancet* into a volume, entitled "Food and its Adulterations, comprising the reports of the Analytical Sanitary Commission of the *Lancet* for the years 1851-54. London, 1855."

In 1855 "The Select Committee on the Adulteration of Food" commenced its labours, and examined as far as possible all those who were likely to have any special knowledge of the adulterations themselves, the methods necessary to detect them, and their effect on the revenue and on health. Dr. Hassall stated to the committee the results of his inquiries both for the *Lancet* Commission and during the course of his other labours, and gave in detail the frauds practised in regard to milk, coffee, tea, drugs, preserved fruits, &c.

Dr. Alphonse Normandy, who had also written a work on adulteration—the result of ten years' investigation—said, in giving evidence as to the aluming of bread, that he had seen alum in bread in crystals of the size of a large pea. "In the bread of one baker I found alum actually in the state of large crystals; I went to him and showed him his bread, and he said, 'I cannot help it.'" In extreme instances he had found as much as from

250 grains to twice that quantity of alum in the 4lb. loaf, and in 1847 he had found magnesia carbonate in three samples of bread. In 1847 and 1848, years of great scarcity, he had discovered bean and pea meal in flour, but this he considered quite exceptional. With regard to beer, he thought that brewers often made use of cocculus indicus; and, finally, he gave evidence of the great adulteration of drugs.

Mr. Blackwell, of the firm of Crosse & Blackwell, gave some very interesting evidence as to the "coppering of preserved vegetables" practised before the food articles appeared in the *Lancet.* The process in use by his firm was to boil the pickles or vinegar several times in copper boilers. After each operation they became greener, and when the proper hue was attained, the process was finished; but since the outcry on coppered vegetables, this process had been abandoned.

Another witness, Mr. O. L. Simmonds, the author of a work upon "Commercial Products," in giving evidence on the adulteration of drugs, estimated that there was a loss to the revenue from this cause of no less than £3,000,000 per annum. As an instance of the manner in which the revenue suffered, he cited the substitution of cassia for cinnamon; cassia paid 1d. per lb. duty, cinnamon 2d. The dealers sold cassia under the name of cinnamon to such an extent as to affect seriously the cinnamon trade.

§ 24. *Adulteration Acts,* 1860 *and* 1872.—Upon the report of the Select Committee, the first general Adulteration Act was drafted, and became law in 1860. The first section enacted, "That every person who shall sell any article of food or drink with which, to the knowledge of such person, any ingredient or material injurious to the health of persons eating or drinking such article, has been mixed, and every person who shall sell as pure or unadulterated any article of food or drink which is adulterated or not pure, shall for every such offence, on summary conviction of the same, pay a penalty not exceeding £5, with costs." A second offence was punishable in addition by publishing the offender's name, place of abode and offence. The Act permitted, but did not compel, the appointment of analysts. The bodies which might appoint such analysts were: in the City of London, the Commissioners of Sewers; in the metropolis generally, Vestries and District Boards; in the counties, Courts of Quarter Sessions. Section 4 provided that any purchaser of any article of food in any of the districts in which analysts existed, might have such article analysed on payment of a sum not less than 2s. 6d. and not more than 10s. 6d.; the purchaser, on the completion of the analysis, was entitled to receive a certificate of the result of the analysis.

These appointments were at first confirmed by the Secretary of State, but afterwards the Local Government Act of 1871 transferred the regulation of the appointments to the Local Government Board. The Act existed, and was in partial operation, for twelve years, when it was entirely recast and interspersed with various sanitary considerations.

In an Act passed in the year 1872 (35 and 36 Vic., c. 74), it was enacted that "Every person who shall wilfully admix, and every person who shall order any other person or persons to admix, any ingredient or material with any drug to adulterate the same for sale, shall be liable to a penalty for the first offence not exceeding £50, with costs." The second offence was punishable by a term of imprisonment not exceeding six months, with hard labour. By the second section "Every person who shall sell any article of food or drink, with which to the knowledge of such person any ingredient or material injurious to the health of persons eating or drinking such article has been mixed, and every person who shall sell as unadulterated any article of food or drink or any drug which is adulterated, shall for every such offence, on a summary conviction of the same, pay a penalty not exceeding £20, with the costs of conviction." By the third section "Any person who shall sell any article of food or drink, or any drug, knowing the same to have been mixed with any other substance, with intent to fraudulently increase its weight or bulk, and who shall not declare such admixture to any purchaser thereof before delivering the same and no other, shall be deemed to have sold an adulterated article of food or drink, or drug, as the case may be, under this Act."

The Act, with doubtful advantage, also extended the right of appointing analysts to boroughs having separate police establishments. The appointment was optional, save on the direction of the Local Government Board. The sixth section provided that inspectors of nuisances or other local officers were to procure samples for analysis. Private purchasers might have articles analysed as before, the only difference being that, under this Act, they were to hand the substance not to the analyst, but to the inspector. There were also provisions as to the sealing and division of samples. Since the Act of 1860 remained unrepealed, the two Acts were both in force simultaneously, and under their joint operation the following offences were punishable :—*

1. Selling any article of food, drink, or medicine, that contains any ingredient injurious to health, and knowing it to contain such ingredient.

2. Selling any adulterated food, drink, or drug.

† "The Law of Adulteration," by Sidney Woolf. Lond. 1874.

3. Wilfully mixing with any article of food or drink any ingredient or poisonous ingredient to adulterate the same for sale.

4. Wilfully mixing any ingredient with any drug to adulterate the same for sale.

5. Selling any article of food, drink, or any drug, knowing the same to have been mixed with other substances with intent fraudulently to increase its weight or bulk, unless such admixture be declared at the time of sale.

§ 25. *The Select Committee*, 1874.—These Acts by no means worked well. Many of the analysts were inexperienced, and even those who had considerable chemical knowledge differed widely in the conclusions they drew from their analyses. The reason of this was evident, for the standards had scarcely been settled. There was, for example, no general agreement as to the amount of "fat" and "total solids" in milk; the question of whether tea should be permitted to be faced, or not, was then (as, indeed, now) unsettled; there was no method in use which distinguished alum added to flour and alumina existing as sand. Analyst contradicted analyst. Magistrates were perplexed as to the meaning of the word "adulteration," and conflicting decisions on mere legal technicalities offered a still further obstacle to the healthy operation of the Act. The public generally were dissatisfied with an Act which on many retail dealers inflicted real hardships—*e.g.*, tea, paid for at the highest market price, and imported direct from China, would be examined by a local analyst, and pronounced to be *faced* with Prussian blue, gypsum, &c.; while, from the peculiar nature of the statute, the seller, however innocent of the fraud himself, could not defend the charge on anything like equal terms. Petitions, moderate in tone, came in from most of the large towns, and the Government decided to appoint another Select Committee. A large number of witnesses: tea merchants, tea brokers, tea retailers, butter merchants, cocoa and coffee manufacturers, milk sellers, bakers, and analysts, were examined by this new Committee in 1874; and on their evidence a report was based, which stated that after having sat fourteen days, and examined fifty-seven witnesses, the Commissioners had arrived at the unanimous conclusion that, while the Act had done much good, it had, at the same time, inflicted considerable injury, and enforced heavy and undeserved penalties upon some respectable tradesmen. "This appears to have been mainly due to the want of a clear understanding as to what does, and as to what does not, constitute adulteration, and in some cases to the conflicting decisions and inexperience of the analysts. Your Committee are, however, of opinion, that the Act itself is defective and needs amendment."

The report went on to say that the adoption of the Act had been by no means general, and in many cases where it had been applied, its operation was of a very restricted character; for, even with competent analysts, if inspectors were not appointed at the same time, the Act remained a dead letter. All the London vestries had made appointments, but in only twenty-six out of seventy-one boroughs, and thirty-four out of fifty-four counties, were there at that date official analysts. The examination of tea was recommended to be made on importation by the Customs. The Committee did not consider that the exact proportion of mixtures need be stated on a label, and they wished to record that mixed mustard and prepared cocoa had been long manufactured at Deptford for the supply of the Navy. They recommended that small districts should be consolidated, and that, as a rule, the boroughs in a county should be united with the county for the purpose of appointing one analyst for the entire district; and they pointed out that the only way to secure "the services of really efficient analysts is to offer them a fair remuneration, which can hardly be done without the union of several Local Authorities in one appointment." The Committee concluded their report by remarking that the public was "cheated" rather than "poisoned."

§ 26. *Sale of Food and Drugs Acts*, 1875 *and* 1879.—On this report was based the Act of 1875, which is at the present moment, with its amendment of 1879, the existing law, and the full consideration of which will be reserved for another Section; the early defect in the Act, however, may be at once alluded to, for it had not been long in operation before its action was almost entirely stopped by legal ingenuity. The sixth section provides that "No person shall sell to the prejudice of the purchaser any article of food or any drug which is not of the nature, substance, and quality of the article demanded by such purchaser;" and in a Justiciary appeal case at Edinburgh, in which an inspector had purchased cream not for his own use but for analysis, the Scotch court discussed the "prejudice" question—three out of seven judges adopting the view that a purchase made under these conditions was not to the "prejudice" of the purchaser, and five out of the seven dismissing the summons on other grounds. The impression produced in this country, however, by the decision of the court, was that the sale, to be effectual, must be made in the ordinary way, and not merely for the purposes of analysis. The same question was raised in quite a different but equally ingenious way in a "mustard case" argued before the Court of Queen's Bench. The purchase in this case was by an officer; the defence being that, as it was well known that mustard was mixed with

flour and other things, such a purchase could not be to the prejudice of the purchaser. The point, however, was left undecided; the question again came before the Court of Queen's Bench, in the case of Sandys *v.* Small, and the "prejudice" question was argued on both points. Whisky was alleged to have been mixed with water, and the defence set up—that it was known to be so mixed, and therefore not to the prejudice of the purchaser—was held by the court to be good, and the case having been decided upon this point, the other was not proceeded with. Finally, the question was settled by the case of Hoyle *v.* Hitchman, March 27, 1879. The facts in this instance were of the simplest character: the appellant had purchased milk in the usual official way; the milk was found to be adulterated, and the defence was that, as he did not use the milk, therefore he did not buy the milk for his own use; he was not prejudiced. The magistrate who heard the case considered the defence good, and dismissed the summons.

Justice Mellor, in giving judgment, observed that the "prejudice" view of the Act "would absolutely nullify its beneficial effect. For if the meaning of the enactment is that the offence cannot be complete without its being 'to the prejudice of the purchaser,' it is hardly possible that the offence should be brought home to any one. And this observation, in my view, goes far to show that this construction cannot be the right one. So far as authority is concerned, there is no direct decision in favour of such a view; and indeed, in the English courts there is hardly any authority upon the point. For in the first of the two cases in this court referred to, the mustard case, my brother Lush distinctly said that, in his view, if the article were adulterated, it must be presumed that it was 'to the prejudice of the purchaser,' and I could not have dissented from that opinion or I could not have concurred in sending the case down to be re-stated on the other point. And as to the other case, no doubt in the course of the argument the Lord Chief-Justice made some such remark, but not by way of a decided *dictum*, and rather by way of query or suggestion, and the decision went upon the other point, so that there is no authority in the English courts in favour of the view now presented. It cannot be said that the weight of judicial authority is against, and I rather think it is in favour of, the view which we have arrived at after the best consideration given to the question, as to the true construction of the enactment. It is quite general in its terms, and its terms are very large, nor is there anything to limit them,—'if any one shall sell, to the prejudice of the purchaser, any article of food not of the nature, substance, or quality of the article demanded by the purchaser.' There is nothing to limit the application of the enactment (as

some of the Scotch judges seem to have supposed) to articles deleterious in their nature. And in several of the sections (13 to 17) provisions are made for purchases by public officers for the purpose of analysis and prosecution, assuming that if the article is found to be adulterated the offence will have been committed. It would be strange indeed if all these provisions were to be made nugatory by a construction which would, in effect, come to this—that proceedings could only be taken by private individuals. Here the purchase was made by the inspector under those sections; but surely the case must be treated as though the purchase had been by a private individual. Now, in the case of a private individual no one could dispute that in such a case as this the offence would have been completed, and the magistrate has so found, in fact. That being so, what difference can it make as to the nature of the offence, that the purchase was by an officer on behalf of the public, and furnished with public money for the purpose? If the purchaser asks for a certain article, and gets an article which by reason of some admixture of a foreign article is not of the nature or quality of the article he asks for, he is necessarily 'prejudiced;' and how can the fact that the purchase is not with his own money at all affect the question of the commission of the offence? The offence intended to be prevented by the Act was the fraudulent sale of articles adulterated by the admixture of foreign substances, which would necessarily be 'to the prejudice of the purchaser;' and those words were inserted only to require that such an adulteration should be shown to have been made. Taking all these matters into consideration, I cannot bring my mind to the conclusion that in such a case as this the offence is less complete, merely because the money with which the purchase was made was not the money of the purchaser, which must be wholly immaterial to the seller, and cannot affect the offence he has committed. I come, therefore, to the conclusion that the magistrate was wrong in dismissing the case on that ground, and, therefore, that the case must be remitted to him to be determined on the evidence as to the offence alleged to have been committed."

Mr. Justice Lush, in expressing his entire concurrence, said that the differences of opinion which unfortunately prevailed as to the true construction of the sixth section of the Act had crippled the operation of a most beneficial Act.—Judgment for the appellant.

Finally, the Act of 1875 was amended by the "Sale of Food and Drugs Act, 1879," which became law on July 21st in that year. This Act settled the "prejudice" question, authorised the obtaining of samples of milk for the purposes of analysis, and

established standards for spirits. (See sections on the "Existing Law relative to Adulteration.")

V.—THE HISTORY OF THE PRESENT SCIENTIFIC PROCESSES FOR THE DETECTION OF ADULTERATION.

§ 27. If an attempt were made to write the full history of the modern system of the practical assaying of foods, beverages, and drugs, the result would be neither more nor less than a history of the development of the chemical, physical, botanical, and medical sciences ; for there has scarcely been a single advance in any one of those sciences which has not some bearing, immediate or remote, on our subject. Hence, the more useful and less ambitious method to pursue will be merely to notice the chief writings and the more noteworthy discoveries of those who have explored this special field of investigation.

The very early and brief notices in the old writers have been already mentioned. The first general works on adulteration were devoted to drugs rather than to foods, and the herbals and the older works contain here and there, scattered through their prolix pages, casual mention of substitutions or falsifications. For example, Saladin of Ascala, a physician to the Grand Constable of Naples, who wrote in the fifteenth century a work on the aromatic principles of drugs, describes methods of preserving food, and in speaking of the adulteration of manna with sugar and starch, cites the case of an apothecary who was fined heavily and deprived of his civil rights.*

§ 28. In the early part of the seventeenth century Bartoletus discovered by analysis milk-sugar (see chapter on "Milk"), and to this epoch belong also some observations and experiments of another Italian, San Francesco Redi† of Florence, published in 1660, on the amount of mineral substances in pepper, ginger, and

* This work, "*Compendium Aromatarium*," was published in Augsburg, 1481. There is no separate copy in the British Museum, but it will be found as the "*Liber Saladini*" in the beautiful folio edition of the Arabic physician (Yúmannâ ibn Massawáih), *Joannis mesuae damasceni medico clarissimi opera, &c., de medicamentorum delectu, castigatione et usu, &c., &c., folio, Venice, 1623.* The work is in the old dialogue style, consisting for the most part of question and answer. The books preceding the "*Liber Saladini*" also contain some observations on adulteration.

† Francesco Redi, 1626–1697; he was at once a poet, a chemist, and a physician.

black hellebore. He burnt 100lbs. of each and weighed the ash: black pepper yielded 5lbs. 2oz. 4drs. of ash, ginger 5lbs. 3oz. 2drs., while black hellebore burnt in the same quantity gave 4lbs. of ash. These ash percentages, as we know, are accurate. He treated the ash with water, and noticed that all the salts lixiviated, and had a peculiar and definite figure, which they kept although they were often resolved and afterwards congealed. "If in one liquid you dissolve together two or three sorts of salts of different figure, when they congeal they all resume their ancient and proper figure." He gives examples of this among mineral salts, and further states that if vitriol of cyprus, rock alum, and nitre, be dissolved, on evaporation and crystallisation the different salts can be readily detected.*

§ 29. The Honourable Robert Boyle, whose numerous writings and discoveries are well known to all scientific men, may be said in a way to have written the first treatise, the sole object of which was to make known a method of detecting adulterations. The title of his work is "Medicina Hydrostatica; or Hydrostatics applied to Materia Medica, shewing how by the weight that divers bodies used in physic have in water, one may discover whether they be genuine or adulterated," 8vo., Lond. 1690. His method of determining specific gravity was similar to that now used. He determined the specific gravity† of pure rock crystal, which he took as a standard, comparing the specific weight of various minerals with it. He showed that impure mercury sublimate, weighed in this manner, would be deficient, and that Roman vitriol mixed with alum might also be similarly detected. He observed that there were several forms of soluble salts in plants, but always some that were cubical. Boyle also determined the percentage of ash in about forty different vegetables, and the amount of soluble ash. Boyle's was not a work of general scope, for the most part confining itself to the recommendation of a particular although widely applicable method.

An early general work on the adulteration of drugs was that of J. B. Vanden Sande,‡ who may be called the pioneer of

* *Phil. Trans.*, 1693, p. 281.

† I believe that the oldest tables of specific gravity extant are those in Lord Francis Bacon's "Historia Densis et Rari," fol., Lond., 1741. A cube of gold was taken as a standard, and cubes of other substances, of a size as exactly similar as possible, were made. He was conscious, however, of the want of complete accuracy.

‡ "*Les falsifications des médicaments dévoilées, ouvrage dans lequel on enseigne les moyens de découvrir les tromperies mises en usage pour falsifier les médicaments tant simples que composées. et où on établit des règles pour s'assurer de leur bonté, ouvrage non seulement utile aux médecins, chirurgiens, apothicaires, et droguistes, mais aussi aux malades.*" Par. J. B. Vanden Sande,

applied quantitative chemistry, for he not only described the mere external characteristics of various articles of the materia medica, but also made alcoholic and ethereal extracts, and determined the weight of the extracts thus obtained. He also, after the manner of his time, distilled the substances and obtained various products.

§ 30. The invention of the microscope, revealing the most intimate structure of animal and vegetable tissues, and the regular and mathematical forms of salts and minerals, gave a great impetus to all the sciences. Antony Van Leeuwenhoek (b. 1632, d. 1723) was the first who in any philosophic manner occupied himself with this instrument. Gifted with rare powers of observation and manipulative dexterity, he made his own microscopes, and prepared all objects with his own hands. His microscopes were what we should now call lenses. Each object, permanently mounted, had a separate microscope, which merely consisted of a small double convex lens let into a socket between two plates riveted together, and pierced with a small hole. The object was placed, if liquid, on a fine little plate of talc, which was then glued to a needle, or, if solid, was attached to the needle itself. There was a mechanical arrangement by which the needle could be depressed or raised, or placed in any position desired. None of his lenses were very powerful—he rather preferred clear definition; nor were they all of the same magnifying power, but varied according to the nature of the object. He possessed an incredible number of these instruments, and at his death bequeathed many of them to the Royal Society. He investigated daily during his long life all kinds of objects in the three kingdoms of nature, and made perhaps a greater number of discoveries as to minute structures than any other man in his time; indeed, there was scarcely a competitor, for the method was peculiarly his own. These discoveries did not attract so much attention in his day as they deserved, the reason probably being that scarcely any one possessed the suitable means of corroborating his researches. Leeuwenhoek seems to have been the first to discover the active principle of tea and coffee, and to describe the structure of the coffee berry.* Speaking of coffee beans, he says: "I placed some of the beans in a proper chemical vessel over the fire, and observed that, in the roasting or burning them, a great quantity of oily substance and also of watery moisture was expelled. The

Maître Apothicaire de Bruxelles, à la Haye, 1784. A well printed 8vo. of 430 pages. The same author wrote a "*Lettre sur la sophistication des vins.*" Amsterdam, and one or two other works.

* The author believes that this is the first notice of the separation of caffeine by Leeuwenhoek.

roasted bean I broke into small pieces, and after infusing these in clear rain water, I suffered the water to evaporate after pouring it from the grosser parts of the coffee, and then I discovered a great number of oblong saline particles of different sizes, but most of them exceedingly minute; all of them with sharp points at the ends and dark in the middle."* He figures these "saline particles," and from the description and the figure they can be scarcely other than crystals of "caffeine" or "theine." He also cut thin slices of the berry, and one of his plates is a very good illustration of the cellular structure of coffee. He noted that "it was of an open and spongy texture . . . and some of the parts which in the figure appear closed up, consisted of globules, and were filled with oil." Still more decisive are his observations on tea, in which it is absolutely certain that he obtained "caffeine" or "theine" by sublimation, for he distilled it and collected the "volatile salt." "All these saline particles were of the same shape, that is, very long and pointed at both ends. . . . I afterwards endeavoured, for my further satisfaction, to discover, if possible, how many saline particles could be produced from a single leaf of tea; but having reckoned up only a part of the volatile salts contained in one leaf, I forbore any further observations, because the number I had already reckoned up was so great that I dared not publish it, as I had proposed to do, and indeed many persons could not believe that the leaf itself could be divided into so many parts visible by the microscope, as I saw volatile saline particles produced from one single leaf." He also examined the ash of tea, and noticed its deliquescent character. He separated several distinct salts, of which one kind had small cubical crystals, and was probably common salt. He also turned his attention to pepper, and extracted from it a crystalline principle, probably "piperine." He powdered long pepper, and placed it in a glass vessel, covering it with rain water to about one-third of an inch. "After the water had stood about two hours, I poured it off, but it being evening I let the water stand all night. The next morning I saw in the place where it was most evaporated an incredible number of saline particles, many of which were almost twice as long as broad, but one side always longer than the other." He also distilled pepper, and extracted from it an oil. He considered the difference between white and black pepper to be that one was decorticated, the other not, and proved that he was right by direct experiment. In speaking of vinegar, he noticed that it was neutralised by chalk, and that it often contains minute eels—these "eels" he figures and describes.

* "The Select Works of Antony Van Leeuwenhoek," 4to. Lond., 1798.

To Leeuwenhoek, then, may fairly be accorded the credit of having made several unnoticed discoveries in food-analysis. Contemporaneously with Leeuwenhoek, Dr. Hy. Power published some microscopical observations, describing the appearances of sand, sugar, and salt, the eels in vinegar, and the mites in oat-meal. He also observed how easy it was to discover the particles or globules of mercury in compound powders. "In those chymical preparations of mercury which they call 'turbith mineral,' 'mercurum vitae,' sublimate precipitate, and mercury cosmetical, you may most plainly and distinctly see the globular atoms of current and quick mercury besprinkled all among the powders, like so many little stars in the firmament."* He also notices the minute structure of several leaves, and may be considered, together with Dr. Hooke,† as the English representative of microscopical science at that date.

Microscopical observers rapidly multiplied as the instrument itself was perfected, and by about the year 1825, really good instruments, although not absolutely achromatic, could be purchased. In 1838, Ehrenberg brought out his great folio on "Infusorial Life." The beauty of the illustrations in this have never been surpassed, and amply prove that very early in the nineteenth century, for those who could afford the expense, there were instruments of great power, precision, and definition.‡

In 1844, Donné§ published his beautiful plates containing, among other things, some accurate representations of the milk

* "Experimental Philosophy, in Three Books, containing New Observation Experiments, Microscopical, Mercurial, Magnetical." Lond., 1663.

† Dr. Hooke published his "Micrographia Illustrata" in 1656, in the *Philosophical Transactions*, in which he made known his invention of glass globules applied to the microscope, by which an immense magnifying power was obtained. He afterwards published a work entitled—"Micrographia; or, Some Physiological Descriptions of Minute Bodies, made by means of Magnifying Glasses, with Observations and Enquiries thereupon," by R. Hooke, F.R.S. London, 1765. The work is a folio illustrated with well executed copper-plates. He describes and figures, like Leeuwenhoek, poppy seeds, vinegar eels, &c. He was a man of great ingenuity and celebrity. In a theoretical manner he anticipated the telephone, for in the preface he says: "'Tis not impossible to hear a whisper a furlong's distance, it having been already done, and perhaps the nature of the thing would not make it more impossible though that furlong should be many times multiplied. . . I can assure the reader that I have, by the help of a distended wire, propagated the sound to a very considerable distance in an instant, or with as seemingly quick a motion as that of light, at least incomparably swifter than that which at the same time was propagated through the air, and this not only in a straight line, or direct, but in one bended in many angles."

‡ *Die Infusionthierchen als Volkommene Organismen.* Von D. Christian Gottfreid Ehrenberg. Leipzig, 1838.

§ A. Donné: *Cours de Microscope.*

corpuscles (see article on "Milk"). Dr. Ure, in an important case in which an attempt was made to evade the duty on cassava starch by calling it arrowroot, and importing it as such, detected the fraud by the microscopic appearances alone. An excellent collection of objects illustrating the minute anatomy of plants was to be found in 1845 in the Museum of the College of Surgeons, the catalogue of which was edited in an illustrated form by Professor Quekett.* About the same time, Quekett also delivered several lectures on histology, in the course of which he pointed out the value of the microscope in the detection of fraud.†

§ 31. In the latter part of the eighteenth and the beginning of the nineteenth century, chemistry advanced with rapid strides: Neumann Caspar ‡ made various experiments on milk, wine, butter, tea, coffee, and other substances; the Boerhave School § analysed milk; Berzelius issued his chemical papers; Scheele instituted a variety of researches, and thus the foundation was being laid of those processes which were improved and perfected by the philosophical mind of Liebig, and applied in the analyses of various vegetable products ‖ by Mulder, many of whose methods are still quoted and taken to a certain extent as standard. This advance in chemical science was naturally accompanied by more elaborate and scientific works on food, and for the first time it became possible to study the subject in a philosophical manner, and to apply a variety of processes for the detection of fraud.

§ 32. There was published, in 1820, a work on the adulteration of food, by Frederick Accum,¶ which is sometimes inaccurately referred to by writers of the present day as "Death in the Pot." Accum, however, wrote no work bearing that title, which belongs properly to a little book by an anonymous writer, to be noticed presently. Accum's work, appearing just at a time when several brewers had been fined heavily for having in their possession illegal substances, and being reviewed most favourably by the press, exercised a very great influence on the public mind

* "Descriptive and Illustrated Catalogue of the Histological Series in the Museum of the Royal College of Surgeons," vol. ii., 1850.

† "Lectures on Histology, delivered at the Royal College of Surgeons, 1850-1."

‡ "The Chemical Works of Neumann Caspar, abridged and methodised." By William Lewis. London, 1773. Neumann Caspar, M.D., vom Thee Caffee, Bier und Wein: Leipsic, 1735.

§ See chapter on "Milk."

‖ "The Chemistry of Animal and Vegetable Physiology, translated from the Dutch." By P. F. H. Fromberg: Edinburgh, 1845.

¶ "A Treatise on the Adulteration of Food and Culinary Poisons, exhibiting the Fraudulent Sophistication of Bread, Beer, Wine, Spirituous Liquors, Tea, Coffee, &c." By Frederick Accum: London, 1820.

—the more so as it was written with considerable ability and knowledge of the subject.

After giving a general review of adulteration, and proving that it was a widespread evil, affecting more or less every industry—that woollen goods were adulterated with cotton, soap with clay, paper with plaster of Paris, provisions of all kinds with a number of worthless, or actually injurious substances, that even hardware, such as cutlery and the like, did not escape—he is surprised at the great ingenuity applied to such bad purposes. "The eager and insatiable thirst for gain," he observes, "which seems to be a leading characteristic of the times, calls into action every human faculty, and gives an irresistible impulse to the power of invention, and where lucre becomes the reigning principle, the possible sacrifice of a fellow-creature's life is a secondary consideration." From generalities Accum then proceeds to describe more or less minutely the fraudulent tricks of each particular trade: "The baker asserts that he does not put alum in his bread, but he is well aware that in purchasing a certain quantity of flour, he must take a sack of 'sharp whites,' a term given to flour contaminated with a quantity of alum, without which it would be impossible for him to produce light, white, and porous bread from a half spoiled substance." He also states that the baker used a powder technically called "stuff," consisting of one part of alum in minute crystals and three parts of salt.

In speaking of brewing frauds he supports his assertions by reference to actual convictions taken from the papers of the day, and he cites among others the King *v.* Richard Bowman, *Times*, May 18, 1818, in which the defendant, a brewer of Wapping, was convicted of having a substance called "multum"* on his premises, and fined £200; and the King *v.* Luke Lyons, in which the defendant was convicted of having various deleterious drugs in his brewery, among which were capsicum and copperas, and fined £420.

From these and similar trials and cases, he gives a list of the adulterations in use by the brewers, among which figure multum (just mentioned), cocculus indicus, sold to tanners and dyers under the name of "black extract," and "bittern," composed of calcined sulphate of iron, extract of cocculus indicus, extract of quassia and Spanish liquorice—a compound not much dissimilar from some of the "hop substitutes" of the present day. He also gives a list of the publicans convicted, between 1815 and 1818, of adulterating beer; these cases were nineteen in number; but the only adulterations proved seem to have been

* *Multum*, a mixture of extract of quassia and liquorice.

"salt of steel," which was doubtless sulphate of iron, common salt, molasses, and the mixing of table beer with strong beer. The fines ranged from £5 to £400.

In a notice of Mr Accum's work in No. 156 of the *Literary Gazette*, there occurs the following passage, which may serve as an example of the spirit of the press:—"Devoted to disease by baker, butcher, grocer, wine merchant, spirit dealer, cheesemonger, pastry cook, and confectioner, the physician is called to our assistance. But here again the pernicious system of fraud, as it has given the blow, steps in to defeat the remedy. The unprincipled dealer in drugs and medicines exerts the most potent and diabolical ingenuity in sophisticating the most potent and necessary drugs—Peruvian bark, rhubarb, ipecacuanha, magnesia, calomel, castor oil, spirits of hartshorn, and almost every other medical commodity in general demand, and chemical preparation used in pharmacy."

A few years after Accum's work a small duodecimo appeared, familiarly known under the name of "Death in the Pot;" but the full title of which was—"Deadly Adulteration, and Slow Poisoning, and Death in the Pot and the Bottle, in which the blood-empoisoning and life-destroying adulteration of wines, spirits, beer, bread, flour, tea, sugar, spices, cheesemongery, pastry, confectionery, medicines, &c., are laid open to the public, with tests or methods for ascertaining and detecting the fraudulent and deleterious adulterations, and the good and bad qualities of those articles, with an *exposé* of medical empiricism and imposture, quacks and quackery, regular and irregular, legitimate and illegitimate, and the frauds and malpractices of pawnbrokers and madhouse keepers. By an enemy of fraud and villany." London.* This little *brochure* of 137 pages, written in a popular style, and rejoicing in a startling title, enjoyed a large circulation, and, despite its small intrinsic

* No date, but probably about 1825. A small Latin work, with a somewhat similar title, had been published about a century previous. *Mors in Olla, seu metallicum contagium in ciborum, potuum et medicamentorum. Schulze:* 1722. This is, however, of but little merit, and only points out the danger of metallic contamination by articles cooked or preserved in copper vessels. At the end is the following:—

"Herr Anhalt zeigt den Tod in Töpfen
Das ist erschröcklich! doch dabey,
Lehrt er! aus welchen Grund man schöpfen,
Soll Gegengift und Artzeney,
Wodurch er dann giebt deutlich zu erkennen
Dass man ihn bald mit Ruhm wird Doctor nennen."

There were besides other "Deaths;" as, for example—"*Mors in vitro seu lethifera vini adusti damna ex sola ejusdem astringendi virtuti contrabeta.* N. B. Noel. 1709. A poor tract, full of words, and offering nothing new.

merit, had more influence on the popular mind than any similar work that had ever appeared. As may be expected from the title, the book is grossly sensational, and in speaking of water, the author says—"The filthy and unwholesome water supplied from the Thames, of which the delicate citizens of Westminster fill their tanks and stomachs at the very spot where one hundred thousand cloacinae, containing every species of filth and all unutterable things, and strongly impregnated with gas, the refuse and drainage of hospitals, slaughter-houses, colour, lead, and soap works, drug mills, manufactories, and dunghills, daily discharge their abominable contents, is so fearful that we see there is no wisdom in the well, and if we then fly to wine we find no truth in that liquid. Bread turns out to be a crutch to help us onward to the grave, instead of being the staff of life. In porter there is no support, in cordials no consolation, in almost everything poison, and in scarcely any medicine cure." In another place he ascribes the sudden deaths of people in the streets, &c., to the adulteration of their food. Among the sophistications of beer he enumerates, following Accum, cocculus indicus, St. Ignatius bean, nux vomica, tobacco, and extract of poppies.

§ 33. About nine years after Accum's book had been published in England, A. Bussy and A. F. Boutron-Charlard published in France a work of considerable merit on the adulteration of drugs,* the arrangement of which is strictly alphabetical. In the preface, the authors assert that the great development in the art of adulteration had taken place particularly since the wars of the Republic and the establishment of the Continental system, and that it was due more especially to the action of the government, who encouraged the use of products of home growth; in consequence of which, roots grown in France were being substituted for those of foreign origin. Chestnut bark, French rhubarb, and poppy were proposed to replace the quinine of Peru, the rhubarb of China, and the opium of the Levant.

Garnier and Harel, in 1844, published their treatise;† a well-written work, moderate in tone, and without exaggeration. A great number of the chemical reactions and tests mentioned by them are in actual use at the present time. Two years later, J. B. Friedrich, in Germany, published his observations on the same subject.‡ The arrangement of Friedrich's work is alpha-

* *Traité des moyens de reconnaître les falsifications des drogues, simples et composées.* Par A. Bussy et A. F. Boutron-Charlard. Paris, 1829.

† *Des falsifications des substances alimentaires et des moyens chimiques de les reconnaître.* Par Jules Garnier et Ch. Harel. Paris, 1844. Small 8vo.

‡ *Handbuch der Gesundheitspolizei, der Speisen, Getränke, und der zu ihrer Bereitung gebräuchlichen Ingredienten.* Herausgegeben von J. B. Friedrich. Ansbach, 1846. 8vo.

betical. He paid much attention to the composition of diseased milk; and although he made little, if any, use of the microscope, the chemical details of the work are superior to any that had hitherto appeared (see article on "Milk").

§ 34. About the same time, after more than twenty years had elapsed since the publication of any English work—Accum's being the last—the subject of adulteration was revived here by John Mitchell,* who published what must be considered a very useful volume, although many of the tests he gives would scarcely stand the ordeal of a court of justice at the present day. He states, *e.g.*, that if an infusion of tea, treated with sulphate of copper, and heated, throws down a copious chocolate precipitate, "hawthorn" is present; if the infusion becomes of a bright green colour on adding caustic soda, sloe leaf† is probable; but if, on the addition of acetic acid, the solution possesses a very bright colour, "its presence is certain." Mr Mitchell's confidence in these reactions is amusing; but, on the other hand, the greater number of his observations are still valid.

§ 35. In 1850 Chevallier issued his dictionary of adulteration,‡ which, through successive editions, has from the time of its appearance been, *par excellence*, the standard French work on the subject. Many years before the publication of his great work, however, M. Chevallier had practically studied the question, as is proved by documentary evidence, and by his numerous representations to the government on the necessity of amending the law. In a petition presented to the National Assembly in 1848, he says §—"Since 1833 I have constantly addressed to the Chambers of Deputies petitions on the same subject, but these petitions have ever been abortive, and fraud has progressively augmented." The first edition of his dictionary, written in a clear style, contained an excellent *résumé* of what was already known with regard to falsifications, and, besides, was enriched with many new facts—the result of a long experience.

In the same year, 1850, Alphonse Normandy, who published the

* "Treatise on the Falsifications of Food, with the Chemical Means employed to detect them." By John Mitchell, F.C.S. London, 1848.

† The belief in the adulteration of tea by the leaves of the sloe is almost contemporaneous with the introduction of tea itself into England, and there are numerous allusions to the practice scattered throughout the various fugitive contributions to literature. However, that tea has been actually adulterated with sloe leaves rests on no direct evidence worthy of consideration.

‡ *Dictionnaire des altérations et des falsifications des substances alimentaires.* Par M. A. Chevallier. Paris, 1st ed., 1850.

§ *Petition sur les falsifications, adressée a l'assemblée nationale.* Par A. Chevallier. 1848.

results of thirteen years' labour in a "Handbook of Commercial Analysis," was one of the first who recommended the use of the microscope for the detection and discrimination of starches: "The admixture of potato flour or fecula with wheat flour may be very well detected by the microscope," p. 210. The scope of his work embraced not only the analysis of food, but also the examination of a variety of commercial substances,* such as ores, agricultural manures, soaps, &c. The arrangement is alphabetical; successive editions have brought the work to the present time.

§ 36. A year after the appearance of Normandy's English and Chevallier's French works, appeared the papers of Dr. Hassall, in the pages of the *Lancet*, as already mentioned. The publication of these papers marked a new era in legal medicine and the investigation of foods, and the technical application of the microscope was fully developed in the English use. It was not so, however, among Continental chemists, for Hureaux, in his "*Histoire dès Falsifications*," published in 1855, scarcely mentions the microscope, although, so far as chemical tests go, his work leaves nothing to be desired. This is the more curious, since the author was aware of the evidence given before the Select Committee, as is obvious from more than one reference.

§ 37. In 1874 a movement took place in England, the effect of which has been to give an extraordinary stimulus to analytical chemistry—viz., the establishment of the Society of Public Analysts. The movement originated with a few of the leading analysts, who, after one or two private meetings, called a general gathering, which all those engaged in actual practice were invited to attend. This meeting took place at the Cannon Street Hotel in August, 1874; and in a few months the society was fully organised, and a definition of adulteration within certain "limits" had been laid down as follows for the guidance of members:—

DEFINITION OF AN ADULTERATED ARTICLE.

An article shall be deemed to be adulterated—

A. In the case of food or drink:—

1. If it contain any ingredient which may render such article injurious to the health of a consumer.
2. If it contain any substance that sensibly increases its weight, bulk, or strength, or gives it a fictitious value, unless the amount of such substance present be due to circumstances necessarily appertaining to its collection or manufacture, or be necessary for its preservation, or unless the presence thereof be acknowledged at the time of sale.

* "A Handbook of Commercial Analysis." By A. Normandy. London, 1850.

3. If any important constituent has been wholly or in part abstracted or omitted, unless acknowledgment of such abstraction or omission be made at the time of sale.
4. If it be an imitation of, or be sold under the name of, another article.

B. In the case of drugs:—

1. If when retailed for medicinal purposes under a name recognised in the British Pharmacopœia, it be not equal in strength and purity to the standard laid down in that work.
2. If when sold under a name not recognised in the British Pharmacopœia, it differ materially from the standard laid down in approved works on Materia Medica, or the professed standard under which it is sold.

LIMITS.

The following shall be deemed limits for the respective articles referred to:—

Milk shall contain not less than 9·0 per cent., by weight, of milk solids not fat, and not less than 2·5 per cent. of butter fat.

Skim Milk shall contain not less than 9·0 per cent., by weight, of milk solids not fat.

Butter shall contain not less than 80·0 per cent. of butter fat.

Tea shall not contain more than 8·0 per cent. of mineral matter, calculated on the tea dried at 100° C., of which at least 3·0 per cent. shall be soluble in water, and the tea *as sold* shall yield at least 30·0 per cent. of extract.

Cocoa shall contain at least 20 per cent. of cocoa-fat.

Vinegar shall contain not less than 3·0 per cent. of acetic acid.

The "proceedings," which appeared first in the *Chemical News*, were afterwards published in the special organ of the Society—the *Analyst*—throughout the pages of which will be found details of numerous processes, discoveries, and improvements in practical chemistry, which it is certain would, for the most part, not have been invented or known had there been no such encouraging organisation. With this brief account of the establishment among us of the Society of Public Analysts, we may bring our sketch to a close.

The following is a fairly complete list of works discussing the adulteration of food as a whole. A list of treatises on single articles will be given in the bibliographies at the end of each chapter.

§ 38.—A LIST OF GENERAL TREATISES ON ADULTERATION CHRONOLOGICALLY ARRANGED.

Boyle, Robert.—"Medicina Hydrostatica; or Hydrostatics applied to Materia Medica." London, 8vo, 1690.

Sande, J. Vanden.—"Les falsifications des médicaments dévoilées." La Haye, 1784.

Favre, A. P.—"De la sophistication des substances médicamenteuses et des moyens de la reconnaître." Paris, 1812, in 8vo.

ACCUM, FRED.—"A Treatise on Adulteration of Foods and Culinary Poisons." London, 1820.

EBERMAYER, CH.—"Manuel des pharmaciens et des droguistes, ou traité des caractères distinctifs des altérations et sophistications des médicaments." Traduction par J. B. Kapeler et J. B. Caventou, Paris, 1821, 2 Vols., in 8vo.

BRANCHI, GIUSEPPE.—"Sulla falsificazione delle sostanze specialmente medicinali e sui mezzi atti ad scoprirli." Piza, 1823.

DESMAREST.—"Traité des falsifications, ou exposé des diverses manières de constater la pureté des substances employées en médecine, dans les arts, et dans l'économie domestique." Paris, 1827, in 12mo.

BUSSY ET BOUTRON-CHARLARD.—"Traité des moyens de reconnâitre les falsifications des drogues, simples et composées, et d'en constater le dégré de pureté." Paris, 1829, 8vo.

WALCHNER, F. H.—"Darstellung der wichtigsten im bürgerlichen Leben vorkommenden Verfälschungen der Nahrungsmittel und Getränke, nebst den Angaben, wie dieselben schnell und sicher entdeckt werden können." Karlsruhe, 1840, in 12mo, 120 pp.

——— ———.—"Darstellung der wichtigsten, bis jetzt erkannten Verfälschungen der Arzneimittel und Droguen." Karlsruhe, 1841, 8vo.

BRUM, FRANZ.—"Hilfsbuch bei Untersuchungen der Nahrungsmittel und Getränke, wie deren Echtheit erkannt und ihre Verfälschungen entdeckt werden können." Wien, 1842.

RICHTER.—"Die Verfälschungen der Nahrungsmittel und anderer Lebensbedürfnisse, nebst einer deutlichen Anweisung die Echtheit derselben erkennen und ihre Verfälschung entdecken zu können." Gotha, 1843.

GARNIER, J., ET HAREL, CH.—"Des falsifications des substances alimentaires, et des moyens chimiques de les reconnaître." Paris, 1844.

BERTIN, G.—"Sophistication des substances alimentaires, et moyens de les reconnaître." Nantes, 1846, 8vo.

FRIEDRICH, J. B.—"Handbuch der Gesundheitspolizei, der Speisen, der Getränke, und der zu ihrer Bereitung gebräuchlichsten Ingredienten." Ansbach, 1846, 8vo.

BECK, LEWIS C.—"Adulterations of Various Substances used in Medicine, and the Means of Detecting them: intended as a Manual for the Physician, the Apothecary, and the Artisan." New York, 1847, 8vo.

ACAM, F. L.—"Traité des falsifications des substances médicamenteuses et alimentaires, et les moyens de les reconnaître." Anvers, 1848, in 8vo.

MITCHELL, J.—"Treatise on the Adulteration of Food." London, 1848, in 12mo.

PEDRONI, P. M.—"Manuel complet des falsifications des drogues, simples et composées." Paris, 1848, in 18mo.

NORMANDY, ALPHONSE.—"Commercial Handbook of Chemical Analysis." London, 1850 (there are later editions).

CHEVALLIER, A.—"Dictionnaire des altérations et falsifications des substances alimentaires, médicamenteuses et commerciales, avec l'indication des moyens pour les reconnaître." Paris, 1850-52, 2 Vols. (last ed., 5th, 1878).

DUNGERVILLE, ÉMILE.—"Traité des falsifications des substances alimentaires, et des moyens de les reconnaître." Paris, 1850.

TAUBER, ISIDORE.—"Verfälschungen der Nahrungstoffe und Arzneimittel." Wien, 1851, 8vo.

PIERCE.—"Examination of Drugs, Medicines, Chemicals, &c., as to their

Purity and Adulterations." Cambridge, Massachusetts, U.S., 1852, in 12mo.

GILLE, N.—"Falsifications des substances alimentaires." Paris, 1853.

FOP.—"Adulteration of Food." London, 1858.

HOW.—"Adulteration of Food and Drinks." London, 1855.

HASSALL, ARTHUR HILL.—"Food and its Adulterations, comprising the Reports of the Analytical Sanitary Commission of the *Lancet* for the years 1851–54." (There is a later edition.)

HUREAUX.—"Histoire des falsifications des substances alimentaires et médicamenteuses." Paris, 1855, 8vo.

MARCET.—"Composition, Adulteration, and Analysis of Foods." London, 1850.

PAYEN.—"Des substances alimentaires." Paris, 1856.

DALTON.—"Adulteration of Food." London, 1857.

SOUILLIER, J.—"Des substances alimentaires, de leur qualité, de leur falsification, de leur manutention, et de leur conservation." Anvers, 1858, 8vo.

KLENCKE.—"Die Verfälschung der Nahrungsmittel, Getränke," &c. Leipzig, 1858.

PETIT LAFITTE.—"Instruction simplifiée pour la constatation des propriétés des altérations et des falsifications, des principales denrées alimentaires." Bordeaux, 1858.

GELLÉE, A.—"Précis d'analyse pour la recherche des altérations et falsifications des produits chimiques et pharmaceutiques." Paris, 1860.

FACEN, AURELIO.—"Chimica bromatologica ossia guida per riconoscere la bontá, le alterazioni e le falsificazione delle sostanze alimentári." Firenze, 1872.

WALCHNER, J. H.—"Die Nahrungsmittel des Menschen, ihre Verfälschungen und Verunreinigung." Berlin. 1875.

An 8vo. of 324 pages, in which there are no plates and nothing new is advanced; it is, however, a not unskilful compilation.

SOUBEIRAN, J. LEON.—"Nouveau dictionnaire des falsifications et des altérations des aliments, des médicaments," &c. Paris, 1874.

The figures are mostly borrowed from Hassall's work, the articles well compiled, French sources predominating, with very scanty notices of German work. At the end of each article there is a short bibliography.

BLYTH, A. WYNTER.—"A Dictionary of Hygiène, comprising the Detection of Adulteration." London, 1876.

HASSALL, A. H.—"Food and its Adulterations, and the Methods for their Detection." London, 1876.

NAQUET, A.—"Legal Chemistry; a Guide to the Detection of Poisons, Examination of Stains, &c., as Applied to Chemical Jurisprudence." New York, 1876.

The work is a translation from the French, but superior to the original. At the end is a useful bibliography of works relating to forensic medicine and adulteration.

SELMI, ANTONIO.—"Chimica applicata all'igiene, alla economia domestica." Milan.

KLENCKE, HERMANN.—"Illustrirtes Lexicon der Verfälschungen der Nahrungsmittel und Getränke." Leipsic, 1878.

SHARPLES, C. H.—"Food and its Adulteration." Preston, U.S., 1879.

BLANE.—"De la Contrefaçon."

DIETSCH, O.—"Die Wichtigsten Nahrungsmittel," &c. Zurich, 1879.

ELSNER, FR.—"Die Praxis der Nahrungsmittel, Chemikers Anleitung zur Untersuchung von Nahrungsmitteln u. Verbrauchsgegenständen, sowie f. hygienischen Zweck." Leipsic, 1880.

PERIODICALS.

Zeitschrift für Untersuchung von Lebensmitteln, &c., Eichstatt.
Zeitschrift gegen Verfälschung der Lebensmittel, Leipzig.
Analyst, London.

VI.—THE PRESENT LAW IN ENGLAND RELATIVE TO ADULTERATION OF FOOD.

THE SALE OF FOOD AND DRUGS ACT, 38 AND 39 VIC., C. 63, 1878; AND SALE OF FOOD AND DRUGS ACT AMENDMENT, 1879, 42 AND 43 VIC., C. 30.

§ 39. The preamble of the "Sale of Food and Drugs Act" repeals the Acts in force relating to the adulteration of food.

Section 2 defines the term food to include every article used for food or drink by man, and the term 'drug' to include every medicine for external or internal use.*

* The Prize Essay of Mr. Wigner, "On a Law to prevent Adulteration in America," contains the following definitive clauses, which are a decided improvement on the English Act, and have been in great part adopted in the American Act:—

A.—IN THE CASE OF DRUGS.

A drug shall be held to be adulterated,

1. If when sold under or by a name recognised in the United States Pharmacopœia, it differs from the standard in strength, quality, or purity laid down therein.
2. If when sold under or by a name not recognised in the United States Pharmacopœia, but which is found in some other Pharmacopœia or other standard work on materia medica, it differs materially from the standard of strength, quality, or purity laid down in such work.
3. If its strength or purity fall below the professed standard under which it is sold.

B.—IN THE CASE OF FOOD OR DRINK.

The article shall be held to be adulterated,

1. If any substance, or any substances, has or have been mixed with it, so as to reduce or lower, or injuriously affect its quality, strength, purity, or true value.
2. If any inferior or cheaper substance, or substances have been substituted wholly or in part for the article.
3. If any valuable constituent of the article has been wholly or in part abstracted.
4. If it be an imitation of, or be sold under the name of another article.
5. If it consists wholly or in part of a diseased, or decomposed, or putrid,

Section 3. No person shall mix, colour, stain, or powder, or order or permit any other person to mix, colour, stain, or powder, any article of food, with any ingredient or material so as to render the article injurious to health, with intent that the same may be sold in that state; and no person shall sell any such article so mixed, coloured, stained, or powdered, under a penalty in each case not exceeding fifty pounds for the first offence: Every offence after a conviction for the first offence shall be a misdemeanour, for which the person, on conviction, shall be imprisoned for a period not exceeding six months with hard labour.

Section 4 is very similar to this, and relates to drugs: "No person shall, except for the purpose of compounding as hereinafter described, mix, colour, stain, or powder, &c., &c., any drug with any ingredient or material so as to affect injuriously the quality or potency of such drug, with intent that the same may be sold in that state, and no person shall sell any such drug so mixed, coloured, stained, or powdered, under the same penalty in each case respectively as in the preceding section, for a first and subsequent offence."

The sections above quoted, formidable as they appear, possess in reality no deterrent powers, but are perfectly harmless, since no prosecution is likely to succeed under these sections, save when supported by very exceptional circumstances; for the next section expressly provides that no conviction is to take place if the person accused "did not know of the article of food or drug sold by him being so mixed, coloured, stained, or powdered," and were able to show that he "could not with reasonable diligence have obtained that knowledge."

§ 40. The real working sections of the Act are the following:—

Section 6. No person shall sell, *to the prejudice of the purchaser*, any article of food or any drug which is not of the nature, substance, and quality of the article demanded by such purchaser, under a penalty not exceeding twenty pounds, provided that an offence shall not be deemed to be committed under this section in the following cases, that is to say:—

1. Where any matter or any ingredient, not injurious to health, has been added to the food or drug, because the same is

or rotten animal or vegetable substance, whether manufactured or not; or in the case of milk, if it is the produce of a diseased animal.

6. If it be coloured, or coated, or polished, or powdered, whereby damage is concealed, or it is made to appear better than it really is, or of greater value.

7. If it contain any added poisonous ingredient, or any ingredient which may render such article injurious to the health of the person consuming it.

required for the production or preparation thereof as an article of commerce, in a state fit for carriage or consumption, and not fraudulently to increase the bulk, weight, or measure of the food or drug, or conceal the quality thereof:

2. Where the drug is a proprietary medicine, or is the subject of a patent in force, and is supplied in the state required by the specification of the patent:

3. Where the food or drug is compounded as in this Act mentioned:

4. Where the food or drug is unavoidably mixed with some extraneous matter in the process of collection or preparation.

In the amended Act, the second section, 41 and 42 Vic., c. 30, states that in any prosecution under the provisions of the principal Act for selling to the prejudice of the purchaser any article of food or any drug, which is not of the nature, &c., it shall be no defence to any such prosecution to allege that the purchaser, having bought only for analysis, was not prejudiced by such sale. Neither shall it be a good defence to prove that the article in question, though defective in nature or substance or quality, was not defective in all three respects.

The sixth section of the amended Act is to be read with the sixth section of the principal Act, for it states that "In determining whether an offence has been committed under section six of the said Act, by selling to the prejudice of the purchaser spirits not adulterated otherwise than by the admixture of water, it shall be a good defence to prove that such admixture has not reduced the spirit more than twenty-five degrees under proof for brandy, whisky, or rum, or thirty-five degrees under proof for gin."

Section 7 of the principal Act enacts that "No person shall sell any compound article of food or compounded drug, which is not composed of ingredients in accordance with the demand of the purchaser; penalty not exceeding £20."

Section 8 provided "That no person shall be guilty of any such offence as aforesaid in respect of the sale of an article of food or a drug mixed with any matter or ingredient not injurious to health, and not intended fraudulently to increase its bulk, weight, or measure, or conceal its inferior quality, if at the time of delivering such article or drug he shall supply to the person receiving the same a notice by a label distinctly and legibly written or printed on or with the article or drug, to the effect that the same is mixed."

Section 9 enacts "That no person shall, with the intent that the same may be sold in its altered state without notice, abstract from an article of food any part of it so as to affect injuriously its

quality, substance, or nature, and no person shall sell any article so altered without making disclosure of the alteration, under a penalty in each case not exceeding £20."

§ 41. One of the chief loopholes which offenders against the Act have diligently availed themselves of is the label section, Section 8. A label will often have a description of the article in large letters, such as C O C O A, C O F F E E, &c., and then in miserably small type a statement that the article is mixed. In the case of Liddiard *v.* Reece, a grocer had sold half a pound of a mixture of coffee and chicory to an inspector; the mixture was contained in a canister, and was duly weighed, and the full price of coffee was paid for it. After the sale had been completed, the purchaser informed the appellant that he intended to have the article analysed. Thereupon, while the packet was still on the counter, the appellant called the purchaser's attention to the label, on which the purchaser noticed for the first time the words "This is sold as a mixture of chicory and coffee," printed in distinct and legible characters. The label was affixed in a conspicuous position on the outside of the packet. The purchaser then said that he had asked for "coffee," and not for "chicory and coffee." The mixture was found by the analyst to consist of 60 parts coffee and 40 parts chicory. On the hearing of the case before the magistrates, they convicted the vendor on the following grounds:—"The fact that the purchaser asked for coffee and was supplied with an article consisting of only 60 per cent. coffee and 40 per cent. chicory, without having his attention called to the label; and without, in fact, seeing it until the purchase was completed, and also the fact that the price he paid for the said article was a usual and fair price for pure coffee, and much more than would have been given for coffee mixed with chicory to the above extent . . . and that, therefore, the appellant was not protected by the said eighth section."

On appeal the case was decided in the Court of Queen's Bench, November 29, 1879, before Justices Lush and Manisty, who quite agreed with the magistrates on their finding, and the conviction was affirmed.*

* This case probably overthrows the case reported in the *Times*, June 8, 1879, Gibson *v.* Leaper, a prosecution undertaken under the old Act, 35 and 36 Vic., c. 74, sections 2 and 3. On conviction the vendor appealed. The case was that of a Spalding grocer, who sold a packet of "Epps's Cocoa" with-

make the oil in the cocoa soluble and easy of digestion, to combine with it arrowroot and sugar. The court quashed the conviction, holding that assuming the cocoa to be adulterated, it had not been sold as unadulterated. In the

From this important decision it is evident, that if a person asks for any substance, such as coffee, and the coffee is handed to him and found to be labelled, such label containing words relative to its being a mixture, yet that such label does not protect the vendor, unless he has previously called the purchaser's attention to it; in like manner, any verbal declaration is no protection unless it is uttered before the sale is completed. The sale, again, is evidently not completed until the goods are delivered into the purchaser's hand, and the vendor has received the money. Should a person buy any substance in a shop, and (after having tendered his money, and the same has been accepted) proceed to state that the article is required for analysis, and the vendor *then* attempt to return the money: if the purchaser does not accept the money, the sale is evidently complete. On the other hand—an inspector went into a druggist's shop and asked for quinine wine. The chemist served him with the wine, wrapped it up, and laid it on the counter. The inspector then produced his bottles, and declaring the nature of his errand, was about to divide the wine into three parts, when the druggist seized the bottle and refused to sell the wine, which, a moment before, by his actions he seemed ready to do. In this case, the sale was not complete. But now, let us suppose that the inspector had been a little quicker than the chemist, and seized the sample, and, notwithstanding the expressed refusal of the druggist to sell, the inspector had cast his money on the counter—Would the drug have been sold? This question is somewhat difficult to answer, but I think that it would have been a sale, and, if adulteration had been proved, the vendor would probably not have escaped through adopting the defence that there had been "no sale."*

In the case of a grocer who sold adulterated coffee, the vendor had received the money, and had laid the packet and also the change

case of Pope *v.* Turle (43, *Law Journal*), May 28, 1874, the Justices of Bedford dismissed a summons for selling adulterated mustard, and the purchaser appealed. It was stated in the case that at the time the respondent delivered the mustard to the appellant he said: "I do not sell you this as pure mustard." The mustard was found to be the common mixture of flour and mustard. Lord Coleridge, Mr Justice Brett, and Mr Justice Grove, were undivided in their opinion that the seller was entitled to their judgment on the ground of his having declared to the purchaser that the mustard was mixed with some other ingredient, and that, even had he not done so, he could not come within the section to incur the penalty, because if the admixture was such as to make it an adulterated article, still he had not sold it as an unadulterated article.

* In any case, the druggist might have been prosecuted under sect. 17 of the principal Act, for refusing to sell.

on the counter, but on hearing the errand of the purchaser he laid his hand on the change and the packet, declaring that the sale was not complete, as he had not given the change, and also that he did not sell the goods as unadulterated. But the magistrates very properly did not admit the defence.

§ 42. There is an important question as to how far a vendor can be protected by having a board in or over his shop or place of business, giving notice to the effect that all the goods are adulterated.

The English law is made for those who cannot read as well as for those who can: and presuming a purchaser to be uneducated, the notice gives him no information. Again, it is certain that a very large number of purchasers, even should the notice be in a conspicuous place, fail to observe it. In most cases in actual practice such notices are a distinct evasion of the Act, being inconspicuous, and in dark corners.

A seller of milk had a van on which a notice was placed, "Country skimmed milk, sold as adulterated milk." The man with his can went on foot from door to door, the van being in the road. It is evident that, in such a case, very few of the customers could have seen the label. An inspector who bought a sample of the milk did not see it, and the magistrate convicted the defendant.* The important appeal case of Sandys *v.* Small, decided before the Court of Queen's Bench, June 25, 1878, bears upon this, and lays down the law. A publican put up a notice in his house: "All spirits sold here are mixed." The inspector of weights sent a messenger to buy some whisky, which was given without anything more being said on either side; but the purchaser admitted that before he bought the whisky he saw the notice, "All spirits sold here are mixed, 38 and 39 Vict., c. 63, sec. 8 and 9," although at the very moment of buying the whisky he did not see it. It was proved that a similar notice was posted at the bar window in full view of persons purchasing. Chief-Justice Cockburn said:—"If the seller chooses to sell an article with a certain admixture, the onus lies on him to prove that the purchaser knew what he was purchasing. With respect to the alteration of the article, the Act has provided him with the means of protecting himself against such a presumption, and says that if he attaches to the article a notice of the alteration which has been made in its quality, then he shall be protected against any charge of an offence against the Act. If he does not resort to this protection, then the presumption of law attaches, and is unrebutted. If he can show that he brought

* *Analyst*, 1880, p. 225.

home by other ways to the knowledge of the customer, that the quality of the article was altered by admixture, then he does not commit the offence, because both parties knew it, and the seller does not sell an article to the prejudice of the purchaser, and the parties are perfectly free to contract on that footing. In that view the seller, if he has stuck up a notice, would not commit an offence though he might not have affixed a label to the bottle, because he did not sell 'to the prejudice of the purchaser.' . . . It was sufficiently manifest that the man who was sent to buy the whisky knew of the notice stuck up, and hence it was clear that the defendant committed no offence."

From this judgment it is sufficiently evident that where the general label or notice has been clearly seen and understood before making the purchase, then no offence is committed. The decision of Liddiard *v.* Reece does not cover exactly the same ground as the case just quoted, but both, I think, support the view here put forward—viz., that the defendant is bound to prove that the purchaser had a clear knowledge of the quality of the goods before purchasing.

§ 43. Section 10 provides for the appointment of public analysts in England, Scotland, and Ireland, by various local bodies, such as, in England, the Commissioners of Sewers for the City of London, the Vestries and Local Boards of the Metropolis, the Quarter Sessions of Counties, and the Town Councils of Boroughs with a separate police establishment; in Scotland, the Commissioners of Supply, or the Commissioners of Boards of Police, or, where there are no such Commissioners, the Town Councils of Burghs; and in Ireland, the Grand Juries of the Counties and the Town Councils of the Boroughs.

These appointments must be confirmed by a central authority, which, in England, is the Local Government Board; in Scotland, one of Her Majesty's Secretaries of State; and in Ireland, the Irish Local Government Board. The appointment is, in the first instance, permissive, but the superintending or central authority may compel the appointment, and the filling of any vacancy appears to be compulsory.

The qualifications of the analyst are, to a certain extent, defined by the Act, for it directs that there shall be appointed "one or more persons possessing competent knowledge, skill, and experience." It has been thought that the person appointed must have had a medical education; but although this may be desirable, and extremely useful, yet it is certain that with regard to the carrying out of the Act itself, the best qualifications are those of a chemical and scientific nature. A board selecting an analyst for the first time should insist more especially on

chemical experience, as evidenced by original papers, the invention of processes of analysis, and practical work done in the laboratory of some well-known analyst. It is a most serious thing for the traders of a town or county to be at the mercy of incompetence or inexperience, and many of the appointments which were at first made under the Act were so notoriously unsuitable, that a great deal of undeserved odium was thrown upon the whole body of analysts. Lately, however, the "survival of the fittest" process has been going forward, with the result of a great improvement, and one likely to be continuous, more especially as the Local Government Board, acting under skilled advice, is now very cautious in confirming appointments, and insists upon proper qualifications.

The eleventh section distinctly lays down the principle of combination, enacting that the town council of any borough may unite with that of any neighbouring borough in appointing an analyst jointly; or the analyst for the county in which the borough is situated may act upon arrangement as analyst for their borough. Those who are practically acquainted with the subject know, that it is only in the largest and most populous places in England that any kind of living can be made out of a public analytical appointment. Hence, it follows that an analyst for a small place must either have private means, or that his chief occupation must be of a more remunerative nature; it is, therefore, highly desirable that the analysis of food and drugs should be in a few hands only, and that an analyst should hold many appointments of the same nature. In this way, and in this way only, will it be possible to have properly fitted laboratories, supplied with all the expensive appliances of modern research, and in this way only will it be possible to improve the processes of analysis. It is also a fact, from the very few cases in which an experienced analyst has to attend as witness, that there would be no inconvenience, were all the northern counties to have their samples analysed at Sheffield, Manchester, or York; the western and south-western counties at Bristol; and the rest of England at the London laboratories. Probably also the whole of the Scotch samples could be dealt with in Glasgow and Edinburgh, and the Irish, in like manner, in two of the chief cities.

§ 44. Section 12 of the principal Act provides for the purchase of samples by any purchaser for analysis by the public analyst for the district in which the purchase is made, on payment to such analyst of a sum not exceeding ten shillings and sixpence; or if there is no analyst appointed for the district, to the analyst of another place. In this latter case the fee appears to be a matter of private arrangement, for the words of the Act are—

"such sum as may be agreed upon between such person and the analyst." In either case, the analyst must give a certificate of his results to the purchaser. The purchaser must also purchase the article in the manner directed in Section 14, as will be shortly detailed.

It is evident that, for legal purposes, the official analyst must be employed, and that under the Act no prosecution can be undertaken except on his certificate. Thus, at the Manchester Police Court, the Milk-Dealers' Protection Society attempted to prosecute on the certificate of a private analyst, but on this technical ground alone the magistrate dismissed the case.*

The author believes that when a purchaser comes to a public analyst with a sample of food, and desires its analysis under the Act, the analyst must assume that the conditions of the purchase under the fourteenth section have been complied with, and cannot refuse to analyse it; on the other hand, if he is expressly informed that the provisions have not been carried out, and moreover that, whatever his certificate may be, there is no intention of proceeding further, then the analyst may refuse to analyse the substance, under the Act, and the question of analysis will be a matter of private arrangement between the purchaser and the analyst; the spirit of the Act being to prevent fraud—not to encourage curiosity.

§ 45. The thirteenth section of the old Act and the third section of the amended Act should be read together:—

"Any medical officer of health, inspector of nuisances, or inspector of weights and measures, or any inspector of a market, or any police-constable under the direction and at the cost of the local authority appointing such officer, inspector, or constable, or charged with the execution of this Act, may procure any sample of food or drugs, and if he suspect the same to have been sold to him contrary to any provision of this Act, shall submit the same to be analysed by the analyst of the district or place for which he acts; or if there be no such analyst then acting for such place, to the analyst of another place, and such analyst shall, upon receiving payment as is provided in the last section, with all convenient speed, analyse the same and give a certificate to such officer, wherein he shall specify the result of the analysis."

By Section 3 of the amended Act the same individuals "may procure at the place of delivery any sample of any milk in course of delivery to the purchaser or consignee, in pursuance of any contract for the sale to such purchaser or consignee of such milk."

Section 4 of the same Act provides a penalty for refusal to

**Analyst*, 1879, vol. iv., p. 74.

submit samples of milk to be taken, of a sum not exceeding £10.

Section 17 of the principal Act also provides a penalty not exceeding £10, for refusal to sell to the persons appointed to carry out the Act any "article of food or any drug exposed for sale, or on sale by retail on any premises, or in any shop or stores. The purchaser shall tender the price for the quantity which he shall require for the purpose of analysis, not being more than shall be reasonably requisite."

Any street or place of public resort is held to come within the meaning of this section.

It is perfectly clear from the sections quoted, that if a sample be taken of milk in transit, that sample must be taken at the place of delivery. If, for example, a milkman is driving his cart through Oxford Street, it would not be legal for an inspector to stop the cart and require a sample of the milk. The sample must be taken at the place where the milk is delivered. This may be a house, or it may be a railway-station, or it may be a public booth where the milk is sold at so much a glass.

From the case of Crouch *v.* Hall recently heard before the Court of Queen's Bench, it is evident that in procuring samples at the place of delivery, the inspector need not divide the sample. The case was briefly as follows:—The inspector was at Euston Station, and saw a can of milk taken from the van. He accordingly demanded and received a sample, and treating the porter as the agent of the respondent, divided the milk into three parts, and gave one of the parts to the porter, telling the latter that he intended to have the milk analysed. He took no steps to inform either the respondent or the consignee of his intention, but on finding the milk adulterated with water laid his information. The case was dismissed by the magistrate, and the inspector appealed. Mr. Justice Field said that the appeal must be allowed. The Court was clearly of opinion that the railway porter was not the agent of the respondent within the provisions of the fourteenth section, nor was he bound to accept a third of the sample of the milk, although he would have been liable to a penalty had he refused to supply a sample. The object of the Act was to secure to the public a supply of pure, unadulterated milk, and for that purpose it was liable to seizure at the time of its being sold by the seller or his agents, provided that a third of the same sample should be tendered to him, so that he might be enabled to have an independent analysis to show whether it was adulterated or not. But as milk had to be supplied from the country, and it was found that a hardship was often inflicted on the London seller, to whom adulterated milk was supplied by farmers, it was

enacted by the Amendment Act of 1879, 42 and 43 Vict. c. 30, that the inspector should have the power of seizing the milk at the place of delivery to the consignee. In this case, although the delivery had not been completed, and although the railway porter could not be held to be the agent of the consignor, the Court was of opinion, that by the Amendment Act the legislature did not intend to extend to the consignor that privilege which was afforded under the previous Act to the seller, namely, that of giving him a third of the sample to enable him to obtain an independent analysis. The case was then remitted to the magistrate in the usual form.

§ 46. Section 14 fully details the method to be pursued by any purchaser under the Sale of Food and Drugs Act.

The person purchasing any article with the intention of submitting the same to be analysed, shall after the purchase shall have been completed, forthwith notify to the seller or his agent selling the article, his intention to have the same analysed by the public analyst, and shall offer to divide the article into three parts to be then and there separated, and each part to be marked and sealed up or fastened up, as its nature will permit, and shall if required to do so, proceed accordingly, and shall deliver one of the parts to the seller or his agent. He shall afterwards retain one of the said parts for future comparison, and submit the third part, if he deem it right to have the article analysed, to the analyst.

Section 15. If the seller or his agent do not accept the offer of the purchaser to divide the article purchased in his presence, the analyst receiving the same article for analysis shall divide the same into two parts, and shall seal or fasten up one of those parts, and shall cause it to be delivered, either upon receipt of the sample, or when he supplies his certificate to the purchaser, who shall retain the same for production, in case proceedings shall afterwards be taken in the matter.

In the case of Horde *v.* Scott, heard in the Queen's Bench division before Justices Lush and Field, on the 4th of May, 1880, it was made clear that an inspector could appoint a deputy. The case was an appeal from a decision of justices in the county of Stafford. An inspector under the Act had deputed his assistant to purchase a sample of coffee, which was duly divided in conformity with the Act, and the analyst certified to its adulteration with chicory. The magistrates, however, considered that as the proceedings were initiated by the inspector in his official capacity, he, having laid the information, and having regard to sections 13, 14, and 17 of the Act, should personally have purchased the article, and the case was dismissed. This,

Mr. Justice Field said, was entirely wrong :—"It did not signify whether the inspector purchased by his own hand or by his agent. Then the magistrates had decided, secondly, that Samuel Toy, being the purchaser, should have submitted the article to the county analyst; there again he thought the magistrates were wrong. . . . If the thing were properly analysed, it does not signify through whose hands the article was bought."

On the purchase of an article it is evidently essential to say, not only that it is the purchaser's intention to have it analysed, but "analysed by the public analyst," care being taken to use the exact words of the Act. This objection has been several times raised with effect. When a deputy purchases samples, it would be a mistake for the inspector to appear and seal the samples. This had better be left to the purchaser, who can then immediately, or at any subsequent period, hand the samples to the inspector, by whom they should be delivered to the analyst. It is obvious that legal proof will be required as to the proper keeping and delivery of the samples.

It has been argued that the division of the sample into three parts means three equal parts; but there is no direction in the Act as to an equal division. At the same time, should the purchaser leave with the seller, or keep himself an insufficient quantity for any further analysis, there would be an infringement of the spirit of the Act; for the purpose of the division evidently is to provide against any mistake or wrong interpretation of facts on the part of the analyst. Should another analysis be required, it would not be right that the seller should be put at a disadvantage by any marked or great inequality in the division of the parts; hence it will be prudent for purchasers to divide the substance into three parts as nearly equal as may be, but it is unnecessary to use for this purpose balances or measures.

On the seller or his agent not accepting the offer of the purchaser to divide the sample into three parts, it becomes the duty of the analyst to divide it into two parts. There is no direct stipulation as to when this is to be done, for the analyst is permitted to keep, if he chooses, the whole, until the termination of the analysis; but it is evidently the course most free from objection to divide it into two approximately equal parts immediately on receipt of the sample, to seal it in the presence of the purchaser, and deliver one of the parts to the purchaser.

§ 47. Section 16 permits articles to be sent by post after being duly registered, and the Postmaster-General has made the following regulations with regard to the transmission of samples:—

"Each packet must be addressed according to the official designation of the analyst, as 'public analyst,' or otherwise; the nature of its contents must be stated on the front of the packet. Any postmaster, at whose office a packet for a public analyst shall be tendered for registration, may refuse to accept it for this purpose, unless it be packed in so secure a manner as to render it at least unlikely that its contents will escape, and injure the correspondence. Liquids for analysis shall be contained in stout bottles or bladders, which shall be enclosed in strong wooden boxes with rounded edges—the boxes being covered by stout wrappers of paper or cloth, and no such packet shall exceed eight inches in length, four in width, or three inches in depth. No packet whatever addressed to a public analyst shall exceed the dimensions of eighteen inches in length, nine inches in width, or six inches in depth. The postage and registration-fee on each packet must be prepaid."

As analyst for a distant county, I have had made a large number of small wooden boxes for the purpose of transmitting samples, and these I have supplied to the inspectors. In this way I have received samples of milk, cream, butter, wines, spirits, and other matters through the post for the last three or four years, and no difficulty has been experienced. There are, however, bulky matters, such as beer, loaves of bread, &c., in which the transmission by post is impossible, and it is a pity that there is not some provision to enable such articles to be forwarded by rail. The inspector having already secured a sample locally, any possible tampering with the article in transit would be easily detected.

§ 48. Section 18 states that the certificate shall be in the form set forth in the schedule, or to the like effect. These last few words are important, for the analyst thereby is not absolutely confined to the certificate in the schedule. Notwithstanding this, it is safer to adhere strictly to the exact form of certificate, and not to attempt to modify it in any way. In certifying, the more definite the certificate is the better. An analyst having given a certificate as follows:—"A sample of coffee was adulterated with 20 per cent. of vegetable matter, which I believe to be chicory," the magistrate dismissed the case, on the simple ground of "the loose wording of the certificate." Probably the magistrate was wrong, for if the words meant anything at all, they meant that the coffee was adulterated with some vegetable ingredient that, whatever it was, was not coffee. Nor do I see that it is essential for the analyst to know the exact nature of a substance added, so long as he is perfectly clear that the substance is foreign to the article, and not of the nature that the purchaser

demanded. It is obvious that coffee may be adulterated by some foreign root which no analyst has ever seen or heard of; and it would surely be a certificate to be accepted and adjudicated upon if the analyst (under these circumstances) were to certify, "This coffee is adulterated with 20 per cent. of vegetable matter which is not coffee, but the exact nature of which is unknown to me." Again, an analyst certified—"Practically, all chicory," and the magistrates dismissed the case on the ground of "the loose wording of the certificate." Here it is probable that the magistrates were right, for such a certificate is neither in the form nor to the effect of the certificate appended in the schedule to the Act, which plainly implies that where there is adulteration, the analyst shall state the percentages of parts. It is true that the case might have been adjourned for the attendance of the analyst, or the certificate might have been amended, but nothing in the Act contemplates or provides for any inaccuracy or carelessness in drawing out the certificate.

In the case of any article liable to decomposition, the analyst must certify specially as to whether "*any change has taken place in the constitution of the article that would interfere with the analysis.*" Milk and butter are specifically mentioned, but the rule would evidently apply to all foods preserved in tins, provided the tin has been opened. It might also be argued that many other substances (such as wine or beer) are liable to decomposition; hence, it will be better for the analyst to give this matter rather a wide interpretation, and insert in his certificate the necessary words, if called upon to certify in reference to any substance that, under any conditions, is liable to decompose. The exact words must be used, for in an appeal heard at the Middlesex Sessions, October, 1880, Peart *v.* Edwards, the analyst certified that the milk was fresh when delivered to him, but omitted to specify whether "any change had taken place in the constitution of the article, so as to interfere with the analysis;" and on this ground the assistant-judge quashed the conviction.

Section 19 provides for the regular quarterly reports of the analyst, copies of which are to be transmitted to the Local Government Board. If, as in many cases, no work at all has been done under the Act, it is evidently the duty of the analyst to send a "*nil*" report.

Section 20 provides for the institution of proceedings. The Act says—"The person causing analysis may take proceedings." He, therefore, need not be the actual purchaser; and it is usual for an inspector to take the summons out on behalf of the public body for which he acts.

In all prosecutions under the Act, and notwithstanding the

section just quoted, the summons must be served within a reasonable time, and in the case of a perishable article, *e.g.*, milk, not exceeding twenty-eight days from the time of the purchase, etc. The summons must state the particulars of the offence or offences, and also the name of the prosecutor; and it must not be made returnable in less than seven days from the day it is served upon the person summoned.

Section 21 of the principal Act provides that the certificate of the analyst shall serve as evidence; therefore, unless specially required, he need not attend. If, however, the defendant require the analyst to be called as a witness, he will then be obliged to appear. This request for the analyst to attend may be by notice from either the solicitor or the defendant himself, or it may be by request in court at the first hearing of the case, in which instance, the case will probably have to be adjourned. Such notice should certainly be given in writing to the analyst, but still it is not advisable to ignore a verbal request.

§ 49. Section 22 provides for a part of the sample, or samples, to be analysed at Somerset House, in case of any dispute as to the correctness of the analysis. The public analysts were much opposed at first to the reference of their work to the laboratory at Somerset House, but it must be confessed that hitherto the clause has worked fairly well; and although mistakes at the Somerset House Laboratory may and perhaps do occur, the work appears to be done there with the greatest care and conscientiousness. Defendants, notwithstanding this clause, are very fond of employing private analysts for the defence: certainly a most unwise proceeding, for if the analysis is disputed, power is given under the Act to refer the matter to a laboratory, which, from the very nature of its constitution, will be perfectly impartial, and the certificate of which will be admitted as evidence.

Section 23 provides for an appeal to Quarter Sessions.

Section 25 gives the opportunity to the defendant to prove by written warranty, "that he had no reason to believe at the time when he sold it that the article was otherwise than of the nature, quality, &c., demanded; that he sold it in the same state as when he purchased it." On proof of this, the defendant may be discharged from the prosecution, but he will have to pay costs, unless he has given notice to the prosecutor that he will adopt this line of defence.

In the case of Rook *v.* Hopley, it was decided that an invoice containing a description of an article sold to a retail dealer is not such a written warranty as is required by Section 25; and a retail dealer who sells an adulterated article in the same state as he purchased it will not, by virtue of such a document, be

entitled to be discharged on being summoned before a magistrate.

Section 26 provides for the payment of penalties recovered, to the authority, for the purpose of defraying the expenses of the Act.

Section 27 has stringent clauses relative to persons convicted of forging warranties, wilfully applying a certificate or warranty of an article of food or drug to any other article of food or drug, the giving of a false warranty, and wilfully giving a label falsely describing the article sold.

This latter clause of the section—viz., "Every person who shall wilfully give a label with any article sold by him, which shall falsely describe the article sold, shall be guilty of an offence under this Act," &c.—would apply to a great many cases of adulteration in which the article is wrongly described by label; but it is evident that guilty knowledge must be proved, for the word "wilfully" presupposes guilty knowledge. In most cases, unless the actual manufacturer were summoned, ignorance would be pleaded.

Section 28 provides that nothing in the Act shall affect the power of proceeding by indictment, or take away any other remedy against any offender under the Act, or in any way interfere with contracts and bargains between individuals, and the rights and remedies belonging thereto, provided that in any action brought by any person for a breach of contract on the sale of any article of food or any drug, such person may recover alone, or in addition to any other damages recoverable by him, the amount of any penalty in which he may have been convicted under this Act, together with the costs paid by him upon such conviction, and those incurred by him in and about his defence thereto, if he prove that the article or drug, the subject of such conviction, was sold to him as and for an article or drug of the same nature, substance, and quality as that which was demanded of him, and that he purchased it not knowing it to be otherwise, and afterwards sold it in the same state in which he purchased it—the defendant, in such action, being nevertheless at liberty to prove that the conviction was wrongful, or that the amount of costs awarded or claimed was unreasonable.

The 30th section of the Act provides for the examination of tea on importation.

The effect of this examination has been so good that adulterated tea, in comparison with the period before the Act, has decreased in a very marked degree.

VII.—THE DUTY OF THE INSPECTOR, OR PURCHASER UNDER THE ACT.

§ 50. It will be the duty of the inspectors appointed under the Act by the local authority employing them, to take and submit samples from time to time to the public analyst, and it will greatly depend on their intelligence and activity whether the Act will be carried out properly or not.

An active inspector, if he is not known when he commences the work, will soon become so, and it will be necessary to employ, as a rule, deputies. The deputies, it is hardly necessary to state, should not be children, but intelligent adults of either sex, and they should be carefully instructed in the "purchase clauses" of the Act, and taught how to seal and properly divide the samples purchased. It will be necessary for the official purchaser to carry with him all materials for properly labelling and sealing samples. A convenient bag with bottles, jars, wrapping paper, wax tapers, matches, sealing-wax, and an official seal, will therefore be essential.

The sample should not be divided, nor any declaration made until the sale is absolutely complete and the sample in possession of the inspector; when that is the case, the exact words of the Act must be used, and he must say, "I have bought this for the purpose of having it analysed by the *public analyst*," and then he must offer to divide it into three parts, which he will at once proceed to do, unless the seller decline to take advantage of the offer; in that case the purchaser will take the whole to the analyst.

The purchaser must carefully note any declaration which the seller may make with regard to the article, and especially whether such declaration is made *before or after* the completion of sale.

The division of the sample must be as equal as possible, and the parts must be very carefully sealed. In sealing bottles, the cork should be driven in flush with the surface of the neck, and the seal not only placed on the top of the cork, but carried round on to the neck itself, so as to render it impossible for a knife to be inserted under the wax and the cork removed without breaking the seal. A label identical in wording and *number* must be affixed to each division of the same sample. In the case of butter and substances which cannot be put into corked bottles, the best method is to wrap the substance, or jar containing the substance, in paper, and put several seals on the paper in such a way that it is impossible for the packet to be tampered with.

The inspector should always carry a copy of the Act with him,

and in case of a refusal to sell, he should then present his card, or declare that he is an inspector duly appointed to carry out the Act, and call the attention of the seller to Section 17, and tender the price of the article sold. If the seller still refuses to sell, then the purchaser evidently has a case under the Act, and should proceed accordingly.

The official purchaser should not select to the exclusion of others the poorest shops, but take samples as equally as possible.

The purchase of samples need not be effected in an officious manner, nor is it just, for example, to enter a shop when full of people, and with ostentation buy and divide the sample before the customers, for an injury may thus be done to an honest tradesman; the people in the shop might naturally think, in such a case, that the tradesman's goods were "things suspect." There are indeed always two ways of doing a thing, and a little politeness and civility will in no way interfere with the execution of duty, or the carrying out of the Act.

The official purchaser will probably be abused occasionally in no measured terms, but he must endeavour to keep his temper, and it is advisable to say as little as possible, and not to retort in any way. The sample retained by the purchaser must be locked up in a drawer or place to which no one else could have access without the key.

Inspectors should from time to time consult the analyst as to what samples would be advisable to take for analysis. There are many substances—*e.g.*, white sugar—which are so seldom adulterated that it is scarcely worth while obtaining samples of such, unless there has been some information laid relative to their quality.

In taking samples of milk in the street, as before stated (p. 55), it is of no use for the inspector to stop the milk-seller while actually carrying his cans from door to door, but he must buy it at a place of delivery; for example, he could not take a sample from an itinerant milk-seller legally while the milk-seller was going from one door to another, but directly the milk-seller stops at any door, he may then demand a sample and tender the money for it, because then the milk is being delivered. He may also go to a railway station, and take samples of milk from the cans themselves; in the latter case, it does not appear necessary to divide the sample into three parts, but the analyst will be obliged to divide it into two, and give the inspector one. (See p. 57.)

PART II.

INTRODUCTORY.

PART II.—INTRODUCTORY.

A DESCRIPTION OF A FEW SPECIAL FORMS OF APPARATUS USEFUL IN FOOD-ANALYSIS.

§ 51. As stated in the first edition of this work, it is no part of the author's plan to describe the elementary apparatus to be found in every text-book, and to be seen in every laboratory. Notwithstanding, it will be convenient here to give a brief notice of some special forms of apparatus useful in food-analysis, which are not figured or described in other works.

APPARATUS FOR THE TREATMENT OF SUBSTANCES BY VARIOUS SOLVENTS.

It is a matter of some moment to economise alcoholic and ethereal solvents, and it is always advantageous to keep a laboratory as free as possible from vapours and odours. Where a solid has to be exhausted by ether or petroleum, one can scarcely imagine anything more convenient than the apparatus invented by Soxhlet, and proposed by him for the purpose of treating milk solids with ether, but in point of fact widely applicable. It consists of a glass tube (fig. 1), the size of which is perfectly under control, and may be made very large or very small, according to individual requirements. For the purpose of milk analysis a capacity of 100 cc. is ample. The tube is quite closed at the bottom, A; the volatile vapours ascend through the tube D, and are condensed in an upright condenser attached to A; the liquid, therefore, falls drop by drop on to the substance at A. When the condensed liquid reaches X, the syphon BB acts, and the whole of the liquid runs into the flask. The apparatus works quite automatically, and scarcely any ether is lost, however long the operation may last.

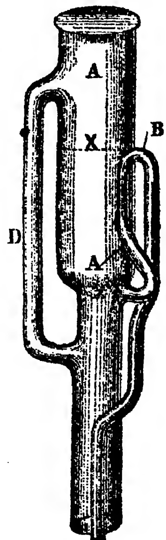

Fig. 1.

Clausnizer has modified this apparatus for small quantities of substances (fig. 2). D is a tube drawn out pipette-like,

J is an inner tube made so as to slip easily into the outer one, and pulled out in the blowpipe flame into a long, almost capillary stem, which is then bent up into a syphon, and terminates in the flask, being made a little longer than the drawn-out portion of D. The mode of action is precisely similar to that just described. The volatile vapour escapes between the two tubes, until it reaches the upright condenser; it is then condensed, and falls in drops on the substance in the inner tube; and when the bend of the syphon is reached, the little tube is at once emptied of the saturated solvent, and the process commences again.

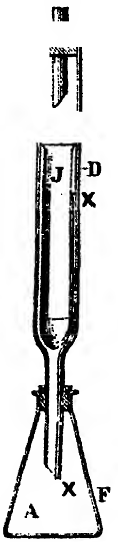

Fig. 2.


Fig. 3.

Another method is as follows (see fig. 3):—Take a flask with a wide neck, fit a small short test-tube, T, into a cork that will go tightly down into the neck of the flask; cut two or three notches in the cork, as shown in the figure. The ether or other solvent continually drops on to the substance in the tube, and when the tube is full, runs over into the flask, and thus the substance is at length exhausted. Similarly, any little apparatus may be suspended from the cork by means of a wire; or, lastly, a little tube may be supported from the bottom by means of a platinum wire-support fused into the flask.

In the Extraction of Liquids by ether, petroleum, &c. the author has found the following apparatus absolutely indispensable, when it is necessary to make, by this means, any quantitative estimations (fig. 4): A is a tube of any dimensions most convenient to the analyst. Ordinary burette size will perhaps be the most suitable for routine work; the tube is furnished with a stopcock and bent tube B, the tube A having a very small but not quite capillary bore. The lower end is attached to a length of pressure tubing, and is connected with a small reservoir of mercury, moving up and down by means of a pulley.

To use the apparatus: Fill the tube with mercury by opening the clamp at H, and the stopcock at B, and raising the reservoir until the mercury, if allowed, would flow out of the beak. Now, the beak is dipped into the liquid to be extracted with the solvent, and by lowering the reservoir, a strong vacuum is created, which draws the liquid into the tube; in the same way the ether is made to follow. Should the liquid be so thick that it is not

possible to get it in by means of suction, the lower end of the tube is disconnected, and the syrupy mass worked in through the wide end. When the ether has been sucked into the apparatus, it is emptied of mercury by lowering the reservoir, and then firmly clamped at H, and the stopcock also closed. The tube may now be shaken, and then allowed to stand for the liquids to separate. When there is a good line of demarcation, by raising the reservoir after opening the clamp and stopcock, the whole of the light solvent can be run out of the tube into a flask or beaker, and recovered by distillation.

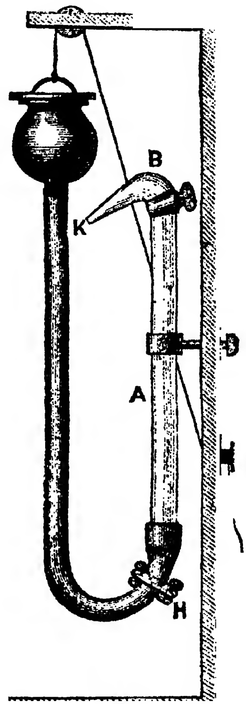

Fig. 4.

For heavy solvents (such as chloroform), which sink to the bottom, a simple burette with a fine exit tube is preferable; but for petroleum ether, ordinary ether, &c., the apparatus figured is extremely useful.

When it is necessary to treat substances in open dishes with volatile solvents, the author uses the following apparatus (see fig. 5), which, since the first description of it in the *Chemical Society's Journal*,* is to be found in most laboratories.

The principle of the arrangement is simply this, that it converts an ordinary dish into a closed vessel, so that ether and volatile liquids may be boiled without loss; or, on the other hand, a volatile liquid may be distilled and recovered with as much ease as in operating with a retort.

The essential part of the apparatus consists of a cast-iron body, R, externally drum-shaped, and having a deep groove, A, in which a little mercury or other "sealing liquid" is placed. Into this groove fits a bell-jar, B, and the part marked D is hollowed out for the reception of a dish. The size of the dish is quite indifferent; any dish will do, so long as it is not too large

* A new and simple Apparatus for the treatment of substances in open dishes by volatile solvents. By A. Wynter Blyth, *Journ. Chem. Soc.*, March, 1880.

for the bell-jar to cover. The neck of the bell-jar is attached to a Liebig's condenser. Should a substance require exhaustion with the solvent, the Liebig is placed in an upright position; should an evaporation or distillation be required, the condenser is placed in the usual slanting position, and in this way all the liquid evaporated is saved. As a matter of convenience it is well to have a pair of these apparatuses in a laboratory, one with an upright, the other with a slant condenser.*

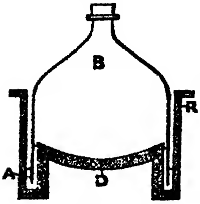

Fig. 5.

§ 52. *The Spiral Balance.*—A spiral balance, proposed and used some years ago by Professor Jolly† (fig. 6), has

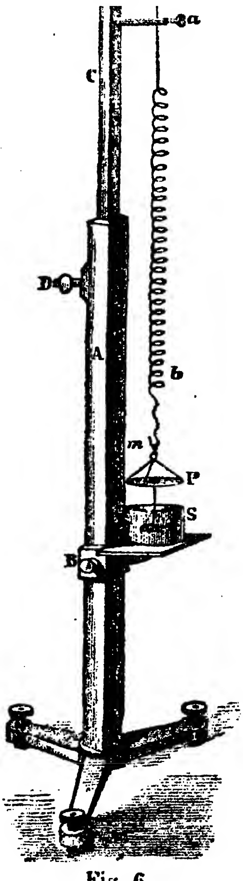

Fig. 6.

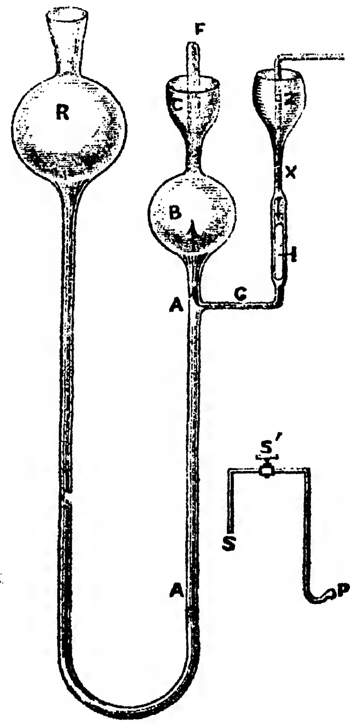

Fig. 7.

* The apparatus can be obtained from Messr Cetti, Brook Street, Holborn.

† V. Jolly, *Sitzungsber Baey. Akad.*, 1864, i. 16

been modified and improved by Mr. C. F. Cross,* and as now constructed is a cheap, accurate instrument, which should find a place in every laboratory, since, for weights up to three or four grammes, its indications are rapid and independent of barometric correction, in short, the "absolute weight" is obtained. The spiral is suspended by means of a binding screw, *a*, to the upright, C, sliding freely up and down the hollow tripod stand, A. The height of this sliding upright is adjustable by a screw, and from the spiral is suspended, by three very thin platinum wires, a mica plate, P; and from the centre of this again, a smooth, thin, metal plate, which is immersed in water, the immersion serving to steady the whole and rapidly bring the index to equilibrium; an opaque glass bead is at *m*, and there is a millimètre mirror scale on A. The bead acts as an index, and its position relative to the scale is ascertained by bringing the eye to that level which makes the bead, *m*, exactly cover its image on the scale. To make an observation, the bead is brought either to the zero of the scale, or to a point sufficiently high to allow of the elongation to be followed on the scale. The calculation required, whether for actual weight or for the specific gravity of a solid or liquid, is sufficiently evident from the following examples given by Professor Jolly in his original paper:—

(*a*.) Determination of original weight, the spiral consisted of 36 turns of piano-wire, No. 6—

Original reading of *m*, ...	2·5
With a load of 1 grm., . . .	374·7
With the object to be weighed, .	213·6

The absolute weight of the latter is, $\frac{213{\cdot}6 - 2{\cdot}5}{374{\cdot}7 - 2{\cdot}5} = 0{\cdot}5671$

with the probable error in the fourth place of decimals.

(*b*.) Determination of specific gravity of a solid—

Original reading of *m*, ...	64·2
Loaded with a crystal placed in pan P, .	275·3
Loaded with a crystal placed in pan S, .	220·8

$$\text{Specific gravity} = \frac{\text{Absolute weight}}{\text{Loss of weight in water}} = \frac{275{\cdot}3 - 64{\cdot}2}{275{\cdot}3 - 220{\cdot}8} = 3{\cdot}8311$$

with the probable error in the second place of decimals.

When the specific gravity of a liquid is to be determined, the lower pan S is removed, and replaced by a small cylinder of glass of about 1 cc. capacity. The loss of weight experienced on submerging the latter beneath the surfaces of the respective

* C. F. Cross, *Chem. News*, Aug. 25, 1881.

liquids is expressed in scale divisions, as in the preceding instances, and the quotients of such numbers are the relative weights.

§ 53. *Vacuum Processes.*—There are a variety of analytical operations, especially those employed in toxicological and food chemistry, which for their proper performance require an efficient vacuum. A short time ago the Sprengel pump was generally employed for this purpose, and, indeed, is so now. Obtaining a vacuum by the Sprengel pump, however, in large retorts or large flasks is a most tedious operation, and as a technical process vacuum working with a Sprengel would become impossible. The author, therefore, uses the same instrument which is employed by the Swan Electric Light Company to exhaust the globes for the thread of incandescent carbon. This pump—the patent mercury pump of Mr. Lane Fox—the author has modified slightly, and with these modifications it is now adapted for every species of laboratory work. The pump (see fig. 7) consists of a glass tube, AA, with a large bulb, B, and a thistle-head, C, in which a ground stopper, F, is fitted, and the whole made tight by a little mercury in C. When gas has to be collected, F is replaced by the apparatus SS′, which consists of thick-walled capillary tubing, having either India-rubber pressure tubing at S′, with a clamp, or a glass stopcock at S′. The side tube, G, is provided with a glass stopper-float, I, ground accurately into X. It allows air or gas to go in the direction of the arrows only, any back pressure carrying up the mercury, and floating and firmly fixing the float into X. In the glass cup, Z, is ground a stopper of angle tubing, with which the apparatus it is intended to exhaust is connected. To work the pump the stopper is taken out of C, and the mercury reservoir, A, is raised until the globe is filled and mercury rises into C. At this moment the stopper is inserted and the reservoir lowered to the ground; this causes a vacuum in the apparatus, and air-bubbles pass into B in the course of the arrows, and collect in the globe. By now raising the reservoir, and at the proper moment loosening the stopper, the air is expelled; on closing the stopper and again lowering, a fresh quantity of air escapes into B, and so on until a perfect vacuum is obtained. A very large retort may be exhausted by working the reservoir up and down about a dozen times, while smaller vessels are made vacuous in three minutes. In collecting gas, as, for example, nitrogen and carbon dioxide in an organic analysis, the stopper F is replaced by the tube SS′P. By dipping the end of the tube P into the mercury trough, having the clamp or stopcock open, and lowering the reservoir, the capillary thread is readily filled with mercury, and the

mercury retained by closing the stopcock. When the combustion tube is vacuous, the beak of the tube is inserted under the eudiometer (or whatever special gas apparatus the analyst has), and the combustion tube made red-hot in the usual way, the gas being readily pumped out and delivered into the eudiometer. The purposes to which such an instrument are applicable are so very various as to render it absolutely necessary in all laboratories.

THE MICROSCOPE, THE SPECTROSCOPE, AND THE ART OF PHOTOGRAPHY AS APPLIED TO THE CHEMISTRY OF FOOD.

§ 54.—There are so many special works describing the microscope* that it will be quite unnecessary to burden the pages of this book with information so readily accessible. The chemist, as a rule, will find a binocular most suitable for his purpose, for it is only with a binocular that it is possible to have a really good view of crystals. Besides, the instrument is so readily converted into a monocular, that it possesses the advantages of the latter combined with its own. For certain branches of research, and more especially for observing reactions under the microscope, the inverted microscope of Dr L. Smith, of Merton College (or those of similar pattern), by which the object glass is placed below the substance to be examined, has this advantage, that it is possible without injury to the instrument, and without being annoyed by acid fumes, to treat substances under observation with strong acids, even at a boiling temperature.

The analytical student will require to familiarise himself with the use of the micrometer and the polariscope. The most suitable micrometer for the measurement of starches and similar substances, is what is called an eyepiece micrometer. A glass, ruled, either in squares, or as a simple scale, is placed between the eye and field piece, so that both the object magnified and the scale are seen clearly at one and the same time. In order to find the value of the divisions of the eye micrometer, it is necessary, in the first place, to determine them by noting how many divisions correspond with one or more of a slip of ruled glass placed on the stage, and containing divisions equalling the hundredths of an inch, or any other convenient measurement.

* The last edition of Dr. Beale's work on the microscope gives a vast amount of information. See also Dr. Carpenter's treatise, the popular work of Mr. Jabez Hogg, &c., &c.

Suppose, for example, that it is found that one-hundreth of an inch on the stage when measured by the eyepiece required 18 of the eyepiece divisions, then it is obvious that each one of the divisions is $\frac{1}{18}$ of $\frac{1}{100}$ or $\frac{1}{1800}$ of an inch; therefore, any object that measured, say four divisions, would be $4 \times \frac{1}{1800} = \frac{4}{1800}$, or would measure the one four hundred and fiftieth of an inch. There is another method of measurement which is extremely accurate and applicable to all cases; this is, to take a micro-photograph of the subject, and to photograph a glass with suitable ruled divisions, with the same arrangements and with the same powers; afterwards a measurement with ordinary compasses can, with great ease and convenience, be made.

Chemical reactions, under the microscope, are either observed in shallow cells ground in the glass slide itself, or simply on the ordinary flat slide, or, as is sometimes convenient, in almost capillary tubes with flattened sides, the microscope being in a horizontal position. Reactions, as a rule, should be observed with only a moderate magnifying power. It is quite possible to execute, on a very small amount of material, a complete qualitative analysis on the stage of the microscope, mixing with drops of the solution under observation droplets of the ordinary test solutions, such as sulphuretted hydrogen water, ammonium sulphide, ammonia, oxalic acid, sodic phosphate, etc. Dr. Beale has recommended glycerine to be used instead of water for these reactions, and he states that although the reactions are slower, yet that they are more perfect.* The method of subliming alkaloids, and its important bearing in the determination of the nature of substances in tea or coffee, is described in the article on "Tea," together with the microscopic appearance of the ash of various leaves, and the method of obtaining "skeleton ashes."

In cutting sections of seeds, leaves, &c., no difficulty is experienced when they are in the entire state, nor are any special instruments required save a sharp razor, for with a little practice sections quite as fine as those it is possible to cut by a section-cutting machine, can be made with a razor. It is, however, quite different with such matters as tea leaves which have been dried and crumpled, or seeds in the state of powder. Here considerable difficulty may be experienced, and it is often not possible to get a section at all satisfactory of any given dark microscopic particle. The author has had tolerably fair results by sprinkling opaque powders on a piece of smooth wood, and embedding the powders in a tenacious glue. When the cement has set, there is no difficulty in getting sections. Similarly, the known processes for

* "How to Work with the Microscope." London, 1880.

embedding soft substances answer well with tea. A simple method is also to gum the leaf, or fragment of leaf, on to a solid substance, and then horizontal sections can be obtained. Sometimes scraping a leaf in the same manner as when a blot is being erased from paper, brings away very beautiful pieces of the epidermis and stomata. Sections of leaves are easily obtained by placing the leaf between two pieces of cork, pressing them well together, and then cutting the finest possible layers with a sharp razor. In all these cases the razor should be wet with some fluid, either water or (which is for the most part better) glycerine, a little diluted. The section floats on the water, and may be transferred to a dish of dilute glycerine. It is well to cut a great number of sections in this way, and select the most transparent from the dish for microscopic examination. The author's new method of observing and preparing leaves is described in the article on "Tea."

§ 55. *Micro-Spectroscope.*—The micro-spectroscope bids fair to become a leading instrument in food-analysis,* more especially since the introduction of so many artificial colouring materials. Fig. 8 shows its various parts. An eyepiece fits into the

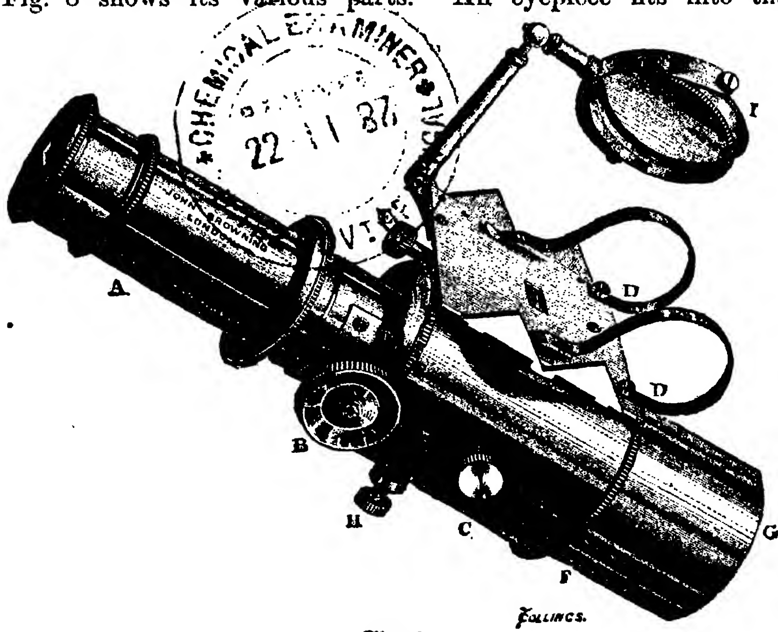

Fig. 8.

* The best micro-spectroscope is that known under the name of the "Sorby-Browning" micro-spectroscope.

microscope tube, having the upper lens made achromatic; at the focal point of this lens is fixed a narrow slit. A small rectangular prism is fixed so as to extend over about one-half of the slit, and reflect the light coming through an aperture. In the stage attached to the side of the eyepiece, the other half of the slit transmits the light, passing up the main body of the microscope through the ordinary object glass.

When all is properly arranged and illuminated, in looking through the lens a narrow line of light is seen, one-half the length of which has passed through an object placed on the stage of the microscope, and the other half through any other placed on the side stage attached to the eyepiece of the prism; and if the prism has been properly adjusted, these two portions should appear perfectly continuous, without any break at their junction; but if not properly adjusted the line appears broken, and would then give false results if the spectra were compared together. The analysing prism is compound, and fits over the eyepiece like a long cap. It consists of two rectangular prisms of crown glass, and two others with angles of 75°, a combination which gives direct vision.

B is a milled head adjusting the focus of the eye lens (fig. 8); C is a milled head for adjusting the slit vertically; H for adjusting the breadth of the slit; D,D are springs for holding a small tube; E is for the purpose of regulating the slit of the second spectrum; F is the position of the field lens of the eyepiece; G is a tube which fits on the microscope. The prisms give that amount of dispersion which is admirably fitted for the purposes to which this instrument is applied, and is in itself sufficient to divide the absorption-bands seen in coloured solids and liquids, while it is not so great as to spread them over too wide a space, and make them obscure, as is the case when the dispersion is great. Since the light which passes through the opening does not extend over the same surface as that which passes through the object glass, it would be far too bright unless modified by means of a small shutter, opening and closing with a screw. In each case this can easily be adjusted so that the light from the two sources is equal, or may be made to vary for some special purpose; there is also a contrivance, so that when very small objects are examined no light shall pass except that which has come through them. (*Sorby.*)

Recent improvements have been made by Mr. Sorby and Mr. Browning, by which every line or band in the spectrum, when being measured, is brought into the centre of the field of view; the jaws of the slit open equally, so that, whatever their width may be, the zero remains unchanged. The micrometer is self-

registering, and the whole turns of the micrometer screw, as well as fractional parts, can be read off at the same time by inspection. The instrument may also be used for opaque as well as transparent objects, and two spectra can be compared at the same time with one lamp. Moreover, the spectrum of the smallest object, or a particular part of any object, may be obtained without difficulty. Mr. Sorby's method of measurement is of the most accurate description. He uses an apparatus giving an interference spectrum, divided by black bands, all of equal optical value. The apparatus is composed of two Nicol's prisms, with an intervening plate of quartz, about ·043 inch quick thick, cut parallel to the principal axis of the crystal, the thickness being so adjusted with the sodium line that the sodium line is exactly at 3·5, counting the bands from the red end towards the blue. He makes use of the following symbols to express the intensity of absorption :—

Not at all shaded.		Blank space.
Very slightly shaded,	. . . . .	Dots wide apart.
Decidedly shaded,	. . . . .	Dots closer.
More shaded,	. . . .	Dots very close.
Strongly shaded, but so that a trace of colour is seen,	- - -	Three hyphens close.
Still darker,	—	Single dash.
Nearly black,	——	Double dash.

Definite narrow absorption-bands are indicated by * printed over their centre. It is assumed that there is a gradual shading off from one tint to the other, unless the contrary is expressed, which is done by means of a small vertical line, as in the following example :—

Normal chlorophyll in alcohol (deep green),

$$\tfrac{7}{8} \overset{*}{—} 2\tfrac{3}{8} - - - 3\tfrac{1}{4} \ldots . \; 4\tfrac{1}{2}\; 6\tfrac{3}{4} \,.\; — — 7\tfrac{1}{2} ——$$

Nothing could be more accurate than Mr. Sorby's method of measurement, and for the actual worker his system of notation will also be found most convenient. For the purpose, however, of graphical illustration, "Vogel's"* method is preferable, and it has been used in this work to delineate various coloured spectra. The system may be at once understood by reference to the diagram (fig. 12). The amount of absorption is shown by curves. Where the curve is highest, there the band is blackest; where it is lowest or absent, the least absorption is present. There is no doubt that the most permanently useful way to express spectra, whether absorption or spark, would be by wave lengths. Then,

* Hermann Vogel: "*Praktische Spectral Analyse.*" Nordlingen, 1877.

however the scales of different spectroscopes might differ (and scarcely two will give the same values), still the results would be the same for all spectroscopes. The following values of wave lengths are sufficient for absorption spectra :—

MILLIONTHS.

A. 760·4	F. 486·0
B. 686·7	G. 480·7
C. 656·2	H. 396·8
D. 589·2	H. 393·3
E. 526·9	

By constructing a diagram similar to the following one,

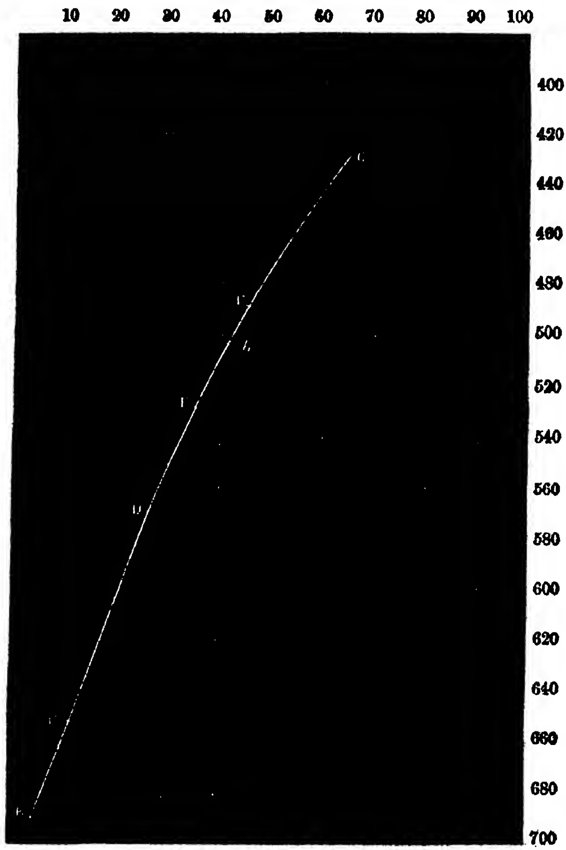

Fig. 9.

only many times larger, having the values of the scale marked

at the top, and intersected by the lines giving wave lengths, and then determining the exact position of Fraunhofer's lines on the scale, and marking them by crosses on the chart as in the diagram, and lastly, joining the points in a uniform curve, it is possible to get very simply the wave lengths of every portion of the scale. The more uniform the curve, the greater the number of lines determined; and the larger the chart, the more accurate are the values. Supposing the centre of an absorption-band to be at 10 on the scale: on referring to

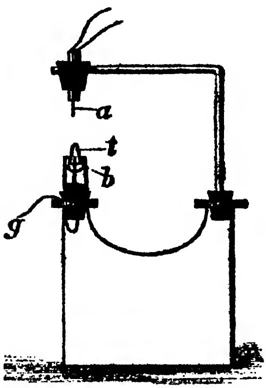

Fig. 10.

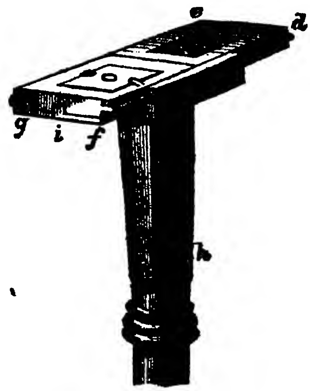

Fig. 11.

the diagram the curve at 10 is exactly cut by the horizontal line 660, therefore, the wave length would be 660, and so on. It will be necessary to measure in all cases the middle of the absorption-band, or the middle of the spark line.

§ 56. The ordinary "spark" spectroscope is not quite so useful to the food-analyst as the micro-spectroscope just described. It will, however, probably be more used when the ash-constituents of food have been thoroughly and scientifically worked out. A very careful search after the rarer metals and elements in the ash-constituents of plants would, in all probability, be rewarded with the discovery of—if not *new* elements—yet of the wide dispersion of the elements that are presumed not to be widely disseminated. The spectroscope in general laboratory use has only been applied to the diagnosis of potash, lithium, copper, barium, strontium, and a few other flame spectra easily obtained without the aid of electricity; but the interesting and convenient method of examination introduced by Lecocq de Boisboudran has made spark spectra so very easy to be obtained by any one who has a battery, and a Ruhmkoff coil capable of giving a good spark, that there is no

reason why an examination of the spark spectra of a body should not become the daily matter-of-course process in all laboratories, and not be restricted to pure scientific inquiry. Boisboudran's method is simply to pass the spark through a solution of the substance to be examined, and for this purpose the following apparatus can be constructed out of the ordinary apparatus of the laboratory (fig. 10).

A Woulfe's bottle is fitted with two good India-rubber corks. In the one a stout glass rod is placed, bent at right angles, serving as a support for a glass tube, through which the wire of the negative pole projects; the other neck carries a little test-tube with the wire *g*, which comes up through the cork, and the test-tube supports a still smaller one, capable of holding a very small quantity of the liquid to be examined; the wire is fused into the bottom of this tube, and terminates a little below the mouth. Over the wire there is a minute tube, somewhat funnel-shaped at the end, which prevents the spark flying to the side of the test-tube; in the larger tube there is a little mercury to ensure contact. One effect of this arrangement is that the lower pole has always a thin film of the liquid over its surface, and on passing the current the spark volatilises the substances in solution, and their characteristic spectra are easily observed.

There are methods of quantitative spectrum analysis proposed by Vierordt and others; but, as yet, they are not sufficiently practical for general use, and the subject requires fresh developments.

§ 57. *Photography.*—The introduction of dry plates and the general simplification of photography will, in a very little time, make its practice general in all the larger laboratories for purposes of registration. In important analyses, likely to entail evidence in the higher courts of justice, it might be useful (and will always be possible) to photograph certain analytical results.

In the quantitative determination of mixtures of starches, a micro-photograph of the mixed starch and the "imitation" mixtures, renders the counting of the number of starches in the field a very easy operation. Similarly, if a measurement of any object be required, a micro-photograph having been taken, and next a photograph of the stage micrometer with the same powers, the object may be measured more easily than in the ordinary way. It is also most useful for the analyst to have by him, in this way, a series of "picture records" for reference. Stein's photographic microscope,* when the object is not to make pretty pictures, nor

* *Das Licht im Dienste wissenschaftlicher Forschung.* Von Dr. Th. Stein, Leipzic, 1877.

to use high powers, is excellent. It merely consists (see fig. 11) of a conical tube, turned out of boxwood, and fastened on to the microscope tube by means of a screw, *h*. Combined with this funnel tube is a wooden tray, in which the frame, *e*, *d*, *f*, *g*, easily slides backwards and forwards. Thin panes of glass are let in the cassette into this frame. Whilst the image is being adjusted, the thin glass, *e*, *d*, stands over the tube, and the prepared plate is put under the little cover at *g*, *f*. If the picture is well defined, the frame, *e*, *d*, *g*, *f*, is pushed into the tray, so that the part, *g*, *f*, can stand over the microscope tube, and by a simple arrangement the photographic plate can be exposed. Direct sunshine will, in most cases, be necessary, and the rays should be transmitted through a cell containing the ammonia-sulphate of copper.

If, however, it is desired to photograph with high powers, the plan recommended and employed by Dr. Woodward, of the Army Medical Museum, Washington, is perhaps the best. The camera box and table are both dispensed with, and the operating room itself is converted into a camera. A room is selected having a southern aspect; the window is provided with shutters on the inside to exclude light, sufficient being admitted through one or two yellow panes to enable the operator to move about freely; a small yellow pane is also let into one of the window-shutters to enable the operator to watch the face of the sky. The microscope is placed horizontally, and a heliostat outside the window throws the direct rays of the sun on to the mirror. The frame of the plate-holder runs on an iron track, ten feet long, and laid on the floor at right angles to the plane of the window. There are most ingenious arrangements for working, although at a distance, the fine adjustment of the microscope; the sun's rays pass through a solution of the ammonia-sulphate of copper.* The fixing of the picture upon the plates, the method of printing from the negatives, &c., are all extremely simple operations (especially to those accustomed to chemical manipulations), and are well described in standard treatises on photography.

§ 58. *Colour.*—It will often be necessary to ascertain the exact colouring-matter used to make articles of food attractive, more especially confectionery, jellies, pickles, &c. The question will generally resolve itself into deciding as to whether the colour is harmless or poisonous, and, if the latter, whether the poison is in sufficient quantity to injure the consumer's health. The poisonous colouring-matters are those containing lead, copper, arsenic, chromium, and zinc, all of mineral origin; together with a few

* The whole arrangement is figured and described in Dr. Beale's work on the microscope.

injurious organic colouring substances, such as gamboge and picric acid. The non-poisonous colouring-matters are the various aniline colours, *so long as they are pure, and contain no arsenic*—saffron, turmeric, annatto, chlorophyll, and generally (with some exceptions) all organic colours obtained from the vegetable and animal kingdoms.

The first thing for the analyst to ascertain is whether the colouring material is insoluble or soluble in water, for, as a rule, with the exception of gamboge, the harmless colours are soluble, while the mineral are insoluble in water. The organic colours are also bleached by a solution of hypochlorite of soda. The aniline colours are soluble in alcohol.

The search for poisonous matters more properly belongs to, and is treated of, in the second volume of this work. With the exception of salts of lead and copper in small quantities, they are rarely met with in food, and even in the matter of confectionery, of late years, there has been a great improvement. As a rule, sweetmeats in England are not coloured with injurious matters.*

The analyst having settled that the colouring-matter is one of organic origin, by its being bleached by sodic-hypochlorite, and by its solubility in water or alcohol, will next proceed to study its spectroscopic characters, either by using a pocket spectroscope, or the micro-spectroscope already described.

Mr. Sorby makes use for his instrument of little cells, cut from barometer tubing. They are half-an-inch long, and with an external diameter of somewhat under half-an-inch; they are ground flat at each end, and cemented with Canada balsam near one edge of a glass plate, so that they may be examined sideways or endways. In examining an unknown colouring-matter, he adopts the following divisions:—

1. Soluble in water, and not precipitated by alcohol.
2. Soluble in water, but precipitated by alcohol.
3. Insoluble in water, but soluble in alcohol.

* This is the more necessary to state clearly, since, on the Continent, very erroneous ideas prevail. Thus, in the *Dictionnaire des Altérations et Falsifications*, par M. A. Chevallier et M. Fr. Baudrimont, Paris, 1878, the adulterations of half a century ago are enumerated; and the reader is informed that the English confectioners not only falsify their sweetmeats with plaster, lime, starch, baryta, but frequently employ bronze powder, the leaf foil of copper, tin, and carbonate and arsenite of copper, verdigris, chromate of lead, red lead, and vermilion; and, further, that nearly all the ginger lozenges contain lead. Similarly, in Dr. Hermann Klencke's *Lexicon der Verfälschungen*, in the article, "*Conditorwaaren*," it is stated that almost all the English confectionery contains lead salts, often to the extent of one and a-half per cent.!! All this is nonsense. Such adulterations have been found, it is true; but instead of being common, they are rare and exceptional.

4. Insoluble in water and alcohol.

He next subdivides his main divisions according to the action of bisulphite of soda.

The organic colouring-matters most likely to be found may be treated of in the order of the spectrum, beginning with the red.

§ 59. Reds.—The common reds are—cochineal, aniline reds, alkanet, and the madder-colours alizarine and purpurine.

Cochineal.—Cochineal is a red complex colouring-matter, secreted by certain species of a peculiar family of insects feeding on the *Cactus coccinellifera*, *C. spuntia*, *C. tunia*, *C. pereskia.* The chief colouring-matter of cochineal is "*carminic acid*," the formula of which appears to be $C_{17}H_{18}O_{10}$. By the action of dilute acids carminic acid splits up into sugar, and a beautiful colour known as *carmine-red*, thus—

$$\underset{\text{Carminic acid.}}{C_{17}H_{18}O_{10}} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Carmine-red.}}{C_{11}H_{12}O_7} + \underset{\text{Glucose.}}{C_6H_{10}O_5}.$$

Cochineal imparts its colouring-matters both to alcohol and water, and is precipitated by acetate of lead, carminate of lead being one of the constituent parts of the precipitate. The solutions of cochineal are purplish-red to crimson, turning a more or less rich violet-purple, with alkalies becoming of a yellow colour on the addition of acids. The colour is well known to chemists, as it is much used as an indicator for acids, being especially useful in titrating an alkaline liquid containing carbonates, since carminic acid is not affected by carbon dioxide like so many other colouring-matters.

Cochineal in neutral solutions gives absorption-bands, but not very definite when examined by the spectroscope; if, however, it be made ammoniacal, then there are bands which differ in position only slightly from the absorption-bands of blood.

No. 18 (fig. 12) is a graphical illustration of the spectrum of cochineal in water; No. 19, in alcohol; and No. 20, on the addition of nitric acid (*a.*) or NH_3 (*b.*). If alum is added to cochineal it loses its power of turning yellow with acids, and the purpurine band becomes so broad that the two bands almost run into each other. On addition of acetic acid they are separated, and appear as tolerably sharply-defined bands between D and E, and there is another at D.

On dissolving cochineal with alum solution, a lake is obtained; on dissolving this in tartaric acid, or dilute nitric acid, the solution gives a band at B and E, and another close on D. The nitric acid solution gives a spectrum very similar to blood.

An aqueous solution of cochineal may be distinguished from the red solutions of brazil-wood, sapan-wood, peach-wood, and a few others, by the fact that the calcium salt of their colouring-matters is violet, and readily soluble in water, while the calcium salt of cochineal-red is dark-purple or almost black, and insoluble in water.

Aniline Reds.—The aniline reds are numerous, but the chief are fuchsine, safranine, and coralline. These three may be

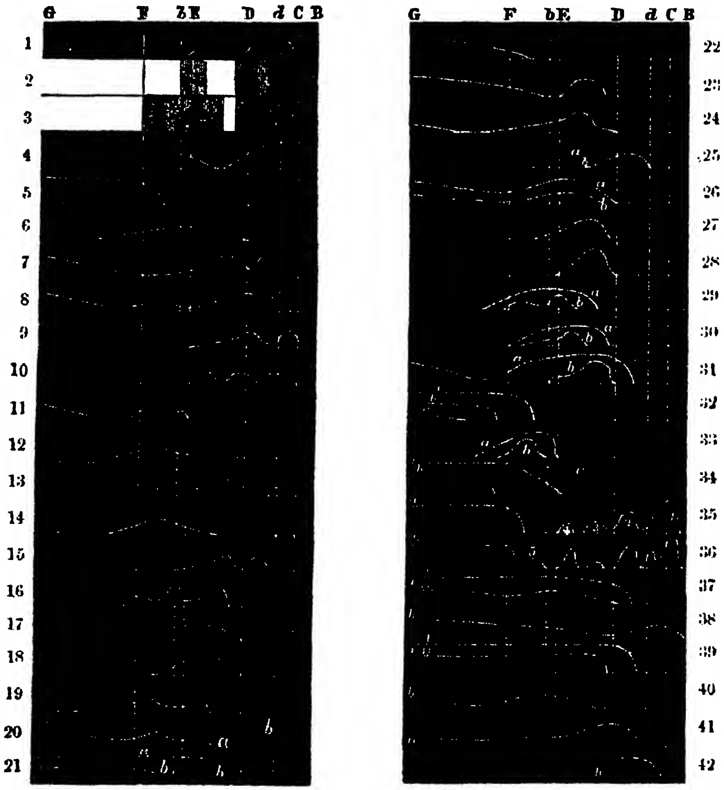

Fig. 12.

roughly distinguished from each other by adding a dilute mineral acid: fuchsine becomes yellow, safranine violet-blue, and coralline gives a yellow precipitate.

Fuchsine, **or** ***Rosaniline,*** in diluted solution gives a spectrum indicated in fig. No. 27. The absorption-band is sharp and decided, and keeps the same place, or very nearly so, whether

No. 1. A diagrammatic representation of the bands of No. 2.
,, 2. Absorption spectra of clear blue cobalt glass.
,, 3. Absorption spectra of dark blue cobalt glass.
,, 4. Diagrammatic representation of No. 3.
,, 5. Alcoholic solution of alizarine.
,, 6. Alcoholic solution of alizarine made alkaline with ammonia.
,, 7. Aqueous ammoniacal solution of alizarine.
,, 8. Alcoholic solution of alizarine made alkaline by potash.
,, 9. Sulphoxanthraquinone in alcoholic solution alkalised by potash.
,, 10. Aqueous solution of sulphoxanthraquinone made alkaline by potash.
,, 11. Alcoholic solution of purpurine.
,, 12. The same alkalised by ammonia.
,, 13. The same alkalised by potash.
,, 14. A neutral solution of alizarinamid.
,, 15. An ammoniacal solution of alizarinamid.
,, 16. A neutral solution of purpurinamid.
,, 17. The same alkalised by baryta.
,, 18. An aqueous solution of cochineal.
,, 19. A dilute alcoholic solution of cochineal.
,, 20. Cochineal in concentrated watery solution with (*a.*) nitric acid, (*b.*) ammonia.
,, 21. Logwood, (*a.*) concentrated watery solution, (*b.*) dilute.
,, 22. The same with the addition of nitric acid.
. . . The same alkalised by ammonia.
,, 23. A decoction of brazil-wood.
,, 24. The same alkalised by ammonia.
,, 25. Litmus, (*a.*) concentrated, (*b.*) dilute.
,, 26. The same made acid, (*a.*) concentrated, (*b.*) dilute.
,, 27. Dilute solution of fuchsine.
,, 28. Alcoholic solution of coralline.
,, 29. Alcoholic solution of eosin, (*a.*) concentrated, (*b.*) dilute.
,, 30. Safranine, (*a.*) concentrated, (*b.*) dilute.
,, 31. Naphthaline red, (*a*) concentrated, (*b.*) dilute.
,, 32. Curcuma, (*a.*) concentrated, (*b*) dilute, (*c.*) strongly diluted.
,, 33. Fluoresceine, (*a*) somewhat concentrated, (*b.*) dilute.
,, 34. Fustic extract.
,, 35. Fresh chlorophyll in alcoholic solution.
,, 36. Old chlorophyll solution.
,, 37. Wine colouring-matter, (I.) pure, (II.) diluted.
,, 38. Wine colouring-matter + NH_3.
,, 39. (I.) Mallow colouring-matter concentrated, (II.) Elderberry concentrated.
,, 40. Acid cherry :—(*b.*) Acid cherry, with addition of tannin.
,, 41. Mallow colouring-matter, with the addition of alum.
,, 42. Indigo solution.

fuchsine be dissolved in water, alcohol, or ether. Diluted acids have no effect on the absorption. It is distinguished from coralline, which gives a very similar spectrum (see No. 28) by the yellow colour with acids already mentioned.

Safranine dissolves in alcohol with a fine rose-red colour, with a weak red fluorescence. Its spectrum is shown in No. 30 (*a*, concentrated solution, *b*, dilute); it is like that of eosin (No. 29), but the spectrum of eosin is changed by nitric acid, that of safranine is unchanged. From a solution containing safranine, safranine may be extracted by shaking it up with its own volume of amyl-alcohol in the tube already described, page 69.

The spectrum of naphthaline-red is figured No. 31. Of these red colours the most likely to be found as a colouring of vegetable juices, &c., is fuchsine.

Coralline, obtained by treating phenol with sulphuric and oxalic acids, and crystallised from alcoholic solution, forms filamentous, interlacing, and lustrous scarlet crystals; or if crystallised from acetic acid, it then forms magenta-coloured rhombic crystals. The crystals are red by transmitted, and dark-green by reflected light; on rubbing they become strongly electric; they are insoluble in carbon disulphide, soluble in phenol, and to some degree in boiling chloroform and boiling benzine. The melting point of the crystals is 150°.

Alkanet, the root of *Anchusa tinctoria*, contains a red colouring-matter, insoluble in water, but soluble in alkalies, alcohol, ether, and fatty oils. The colouring-matter appears to be an acid, anchusic acid, $C_{35}H_{40}O_8$. In dilute solutions the spectrum shows three absorption-bands; on the addition of a trace of a magnesium salt, a fourth absorption-band appears, hence alkanet-red is a test for magnesium salts, and conversely a magnesium salt is a test for alkanet-red.* It may not unfrequently be found as the colouring-matters of tooth tinctures, hair oil, &c.

Madder.—The root of the madder, *Rubia tinctorium*, contains two colouring-matters—alizarine and purpurine—with others less studied.

Alizarin, $C_{14}H_8O_4$, crystallises from an alcoholic solution in yellowish-red crystals, and may be sublimed as brilliant red needles at temperatures a little above 100°. The needles are sparingly soluble in water, but dissolve freely in alcohol and ether. Alizarine is now made artificially on a large scale. The

* Magnesium salts also alter more or less characteristically the spectrum of juice of elder berries, the colouring-matters of the beet, dahlia, dragon's mouth, horse chestnut, hyacinth, violet, rhododendron, purple aster, and *primula farinosa*. *Bericht der Deutsch. Gesellschaft*, xiii., 766–768.

alcoholic solution of artificial alizarine shows no bands, but there is extinction of the violet up to the green (see No. 5). On the addition of ammonia the solution changes to a beautiful red, with weak bands in the green (No. 6); the aqueous ammoniacal solution gives two bands (No. 7); the alcoholic solution made alkaline with potash gives evidence of a third feeble band (No. 8). Natural alizarine is not now much used, but it may be at once distinguished from the artificial by its giving absorption-bands in an alcoholic solution.

Alizarine may be also distinguished by chemical tests: copper acetate added to a solution in alcohol gives a purple precipitate, aluminium acetate gives a red precipitate in an alkaline solution, and ferrous acetate and other iron salts give a dark blue violet precipitate. Blue precipitates are also formed on the addition of either barium chloride or calcium chloride to alkaline solutions. These precipitates have respectively the composition $C_{14}H_6O_4Ba$ and $C_{14}H_6O_4Ca$.

Purpurine, $C_{14}H_8O_5$, crystallising from an alcoholic solution in yellow needles, and subliming like alizarine in red needles, dissolves in alkalies with a dark red colour; it gives not blue but purple precipitates with the chlorides of calcium or barium. The alcoholic solution gives (see No. 11) weak absorption-bands at F and at BE. The spectrum on the addition of ammonia or potash becomes very characteristic (see Nos. 12 and 13).

Safflower.—The safflower, *Carthamus tinctorius*, contains in its petals several colouring-matters, chief among which is carthamine or carthamic acid, $C_{14}H_{16}O_7$. Carthamine turns red in alkaline solutions, and may be precipitated red by an acid. It is met with usually as a delicate pink or red dye, and forms the usual colouring-matter of rouge.

Logwood contains a colouring-matter named *hæmatoxylin*, $C_{16}H_{14}O_6 + 3H_2O$, crystallising from water in yellow prisms; this changes by the action of the air and ammonia into a red or purple substance named *hæmatein*, $(C_{16}H_{13}O_6)_3N$. It may also be produced by adding nitric acid to an ethereal solution of hæmatoxylin. Hæmatein always exists in the free state in the wood, and an alcoholic tincture gives the reaction of hæmatein. The spectrum of the logwood colouring-matters is delineated in Nos. 21, 22, and 23. Alkalies turn the tincture first red, and then violet. The best test, however, is the addition of an aluminous salt to an ammoniacal tincture of logwood, the result being the formation of an abundant bluish violet precipitate. This reaction is made use of in the testing of bread for alum.

Brazil-wood, sapan-wood, lima-wood, peach-wood, and some others, yield a glucoside, which splits up into sugar and *brasiline*,

$C_{22}H_{20}O_7$. Alkalies turn brasiline a crimson colour, and the crimson solution gives blackish violet precipitates, with aluminium and stannic salts. It is oxidised slowly in the air, or rapidly by the action of nitric acid into a red crystalline body, *brasilein*, $(C_{22}H_{19}O_7)_3N$. The spectrum of brazil-wood extract in solution is delineated in Nos. 23 and 24.

There is also a red colouring-matter yielded by the santal wood, named "*santalin*," and occurring in microscopic red crystals insoluble in water, but dissolving in alcohol, with a red colour, turning to violet on the addition of alkalies.

§ 60. Orange and Yellow.—The most common oranges and yellows are the annatto colours: curcuma, picric acid, fustic, chrysophanic acid, gamboge, aniline orange, and naphthaline yellow.

The *Annatto Colours.*—The colouring-matters of the annatto are two substances, one a yellow, *orellin*; another a cinnabar red substance, *bixin*. The latter is described in the article on "Annatto." The annatto colouring-matters are not soluble in water, but are easily dissolved by alcohol. The alcoholic solution is orange red, and non-fluorescent. On the addition of nitric acid it becomes turbid. On dilution with water, there is a strong fluorescence, and it becomes yellow-green. It then absorbs, like ferric chloride, the whole left side of the spectrum E, and half to D.

Turmeric is the root of *Curcuma longa.* The colouring-matter is *curcumin*, $C_6H_{10}O_3$, insoluble in cold water, and sparingly soluble in boiling water. It is very soluble in alcohol, and forms brilliant yellow crystals. Turmeric moistened with boric acid and dried assumes an orange colour, changed by alkalies into a blue; this is due to the formation of a compound soluble in alcohol, forming a red solution, and crystallising in lustrous green crystals, to which the name of *rosocyanin* has been given. No. 32 shows the spectroscopic appearances of curcumin.

Picric Acid $(C_6H_3(NO_2)_3O)$, also called *carbazotic acid* and *trinitrophenol*, is formed commercially by acting on phenol, by dissolving it in sulphuric acid, and then treating the solution with nitric acid. It crystallises from hot water in yellow plates, having a very bitter taste. The salts are explosive. It is taken up from acid watery solutions by petroleum-ether, ether, or benzine, and hence can be readily obtained pure enough for examination.

Picric acid is not precipitated by acetate of lead. The chief chemical test is the production of isopurpurate of potash, which is the result of adding cyanide of potash, and gently warming.

The reaction is represented as follows :—

$$C_6H_3(NO_2)_3O + 3CNK + 2H_2O = C_8H_4N_5O_6K + CO_3K_2 + NH_3.$$

Isopurpurate of potash is of a blood-red colour.

Fustic is the general name for yellow colours found in the wood of the *Morus tinctoria.*

The wood contains two distinct colouring-matters; the one, *moritannic acid,* $C_{13}H_{16}O_6 + H_2O$, soluble in hot water, and forming yellow crystals; the other, *morine,* $C_{12}H_8O_5$, is but sparingly soluble in water; crystallised from alcohol the substance forms yellow needles. Both give yellow precipitates with acetate of lead. The spectroscopic appearances of fustic are shown in No. 34 (*a.*) in concentrated, (*b.*) in dilute solution.

Chrysophanic Acid, $C_{15}H_{10}O_4$, appears to be dioxymethylanthraquinone. It is contained in the rhubarb and wall lichen (*Parmelia parietina*). In commerce it is in the form of six-sided tabular crystals, of a pale to an orange-yellow colour. It is very readily extracted from rhubarb which has been previously macerated in water, pressed, and dried, by digesting the rhubarb in benzine. The crystals are soluble in ether, oil of turpentine, coal-naphtha, benzine, and other hydrocarbons.

The spectrum of chrysophanic acid is very similar to that of natural alizarine. Solutions of chrysophanic acid give, with alkalies, a rich purple colour. An ammoniacal solution of chrysophanic acid yields, with alum, a beautiful rose-coloured precipitate. An alcoholic solution of subacetate of lead gives, in the alcoholic solution, a red-white precipitate. Chrysophanic acid, on being oxidised with nitric acid, yields methylanthraquinone, $C_{15}H_{10}O_2$.

Gamboge.—This is a colouring-matter derived from the *Garcinia morella,* var. *pedicellata.* It is a gum resin, to which the formula of $C_{30}H_{35}O_6$ has been ascribed. It is very insoluble in water, but soluble in alcohol.

In order to detect it in sweetmeats, to which it has occasionally been added, the yellow colouring-matter is dissolved in alcohol, and precipitated by water, a reaction at once showing that it is of a resinous nature. The precipitate, if gamboge, will give a red colour with an alkali. It is without doubt a poisonous colour, but the question of quantity must be considered. Sixty grains has caused death, and five grains is a medicinal doze; and since some persons, especially children, are peculiarly susceptible to the action of medicines, even quantities so small as a third of a grain in a couple of ounces of sweets, should be considered as having possibly an injurious action.

The *aniline yellows* and *oranges* may be distinguished from the colours just described by the tests described in the general scheme at page 93.

§ 61. The GREENS—are chlorophyll and the aniline greens.

Chlorophyll, the green colouring-matter of plants. It would appear that it is now possible to separate chlorophyll in a crystalline state. The merit of this discovery belongs to A. Gautier, who crystallised chlorophyll in 1877,* and two years afterwards Hoppe-Seyler,† without knowing of Gautier's paper, described the same substance under the name of chlorophyllone. Gautier's method is as follows:—The leaves are pounded in a mortar, and sodic carbonate added in quantity nearly sufficient to neutralise the acid juices, and the product strongly pressed. The marc is then exhausted at 55°, and again strongly pressed; to the exhausted substance alcohol is added, and the whole digested at 83°; chlorophyll, wax, pigments, fat, and other matters dissolve. The liquid is filtered and digested with coarse animal charcoal, which has been previously washed. At the end of four or five days it has lost its green colour, and becomes yellowish- or brownish-green. The charcoal retains the chlorophyll, and is now washed with alcohol at 65°; the latter removes a yellow crystallisable substance generally accompanying chlorophyll, and intimately allied to it in composition.

From the animal black thus freed from the yellow substance, chlorophyll may be extracted by anhydrous ether, or very light petroleum ether. A slow evaporation in the dark will yield it in crystals. Thus obtained, chlorophyll forms flat, often radiating crystals, which may be more than a centimetre in length, soft in consistence, and of an intense green colour when recent, but slowly changing to yellowish-green, or greenish-brown. If the crystallisation is too rapid, these long crystals are not obtained, but green masses composed of microscopical crystals, belonging to the rhombohedral system.

Diffused light changes chlorophyll to yellowish-green, and ultimately decolourises it. The crystals dissolve in ether, chloroform, petroleum, carbon disulphide, and benzine. Digested with hydrochloric acid, chlorophyll splits up into two new substances, one giving a beautiful blue solution, the other remaining insoluble, but dissolving with a brown colour in hot ether and alcohol, from which it appears inclined to crystallise. Fremy, who was the first to notice this splitting-up of chlorophyll, called the first substance phyllocyanine, and the last phylloxanthine.

* *Bulletin de la société chem.* T. xxviii., 1877, p. 147. *Comptes rendus*, lxxxix., p. 861.

† *Bericht der Deutschen Chem. Gesellschaft*, 1879.

The ultimate analyses of chlorophyll by Hoppe-Seyler and Gautier agree fairly well, especially as Hoppe-Seyler's chlorophyll being derived from monocotyledonous and Gautier's from dicotyledonous plants, it is possible there may be some slight difference in their composition. Chlorophyll has not yet been obtained free from ash.

	Hoppe-Seyler.	Gautier.
Carbon, ...	73·4	73·77
Hydrogen, . . .	9·70	9·80
Nitrogen, ...	5·62	4·15
Phosphorus, . .	1·37	
Phosphates, Ash, .		1·75
Magnesia, ...	·34	
Oxygen, ...	9·57	10·33

Mr. Sorby has studied the colouring-matters of leaves, and has divided them into five groups :—1, Chlorophyll ; 2, xanthophyll ; 3, erythrophyll ; 4, chrysophyll ; and 5, phaiophyll.

The *Chlorophyll* group are all green in colour ; the members are insoluble in water, but soluble in alcohol or carbon dioxide. The absorption-band is in the red, but the green is more or less completely transmitted, so that the prevailing tint is a more or less modified green. There appear to be several members of the group, one kind (which is probably the crystalline chlorophyll just described) occurs nearly pure in small aquatic plants, allied to the Oscillatoria ; the green leaves of plants contain this, along with one which gives special absorption-bands. A third kind is the result of the action of acids on this, found more especially in autumnal leaves which have become brown. A fourth is in faded Confervæ, and turns blue when acted upon by hydrochloric acid (Fremy's phyllocyanine ?)

Xanthophyll.—This is a group of orange colours. They are insoluble in water, but soluble in alcohol or carbon disulphide. The general tint of the spectrum is orange, there is absorption at the blue end, often more or less marked narrow bands. These bands are best seen in carbon disulphide solution. Examples of two species of xanthophyll are the inner and outer layers of the common carrot.

Erythrophylll.—A group of reds. They are soluble in water and weak alcohol, but not in carbon disulphide. There are many varieties. There is a strong absorption in the green parts of the spectrum.

Chrysophyll is a golden-yellow colour, soluble in water and weak alcohol, like the last, and insoluble in carbon disulphide.

The *Phaiophyll* group consists of various browns, due to the oxidation of chlorophyll. They give no definite absorption-bands.

The spectrum of chlorophyll is delineated in Nos. 35 and 36. No. 35 is an alcoholic solution of fresh chlorophyll. There are two well-defined absorption-bands in the red, and two others, somewhat weaker, between E and D. The blue end of the spectrum, up to F, is dark. Old solutions (No. 36) alter the bands somewhat, and a fifth band appears between F and C.

Green, if not due to chlorophyll, nor to colouring-matters of copper or metallic origin, will probably be aldehyde green, or iodine green, or the chlorinated derivative of the latter, which is said to be an equally good tinctorial agent.

These may be distinguished by the tests in the general scheme given farther on.*

§ 62. INDIGOS AND VIOLETS.—The chief blues to be found, not of mineral origin, are indigo, litmus, and the aniline colours.

Indigo.—Indigo is the produce of a great number of plants, most of which belong to different species of *Indogifera*. It would seem that the indigo exists in these plants in the form of a syrupy glucoside, which has been named *indican*, and splits up into *indiglucin* and *indigo-blue*, according to the equation,

$$\overbrace{C_{52}H_{62}N_2O_{34}}^{\text{Indican.}}\ \overbrace{4H_2O}^{\text{Water.}} = C_{16}H_{10}N_2O_2 + 6C_6H_{12}O_6.$$

In the treatment of the crude substance by acids, other red and yellow colouring-matters are thrown down with the indigo. Pure indigotin has to be freed from these impurities, and may be crystallised in minute crystals. It is also capable of sublimation.

Crystalline indigotin is of a deep purple colour, and is insoluble in water, dilute acids, and alkalies. It is converted into orange crystals of *isatin*, $C_{16}H_{10}N_2O_4$, by treatment with oxidising agents. Indigotin is dissolved in concentrated sulphuric acid, and two compounds are formed—the one, *indigo monosulphonic* acid, or *indigo-purpuric* acid, $C_{16}H_9N_2O_2(SO_3H)$, which is first formed; and the other indigo disulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, which is formed later. The first is easily separated from the second, for it is precipitated by the addition of water. A sodium salt of indigo-sulphuric acid is used much in laboratories under the name of indigo-carmine as a test for nitrates, as well as for their estimation, oxidising agents converting it into *isatin-sulphonic* acid, $C_{16}H_8N_2O_4(SO_3H)_2$, which has an orange colour; hence, when a liquid containing a nitrate is acidified strongly

* Rinman's green may be met with; it essentially consists of oxide of zinc, coloured with oxide of cobalt. Sometimes arsenic is used in its manufacture; if arsenic free, and in small quantity, it is a harmless colouring material. There is also an aniline green which is a compound with zinc chloride.

with sulphuric acid, and a solution of indigo-carmine run into the hot solution, the colour changes at first to yellow until an excess of indigo has been added. The spectrum of indigo, in concentrated solution, is shown in No. 42. There are no bands, but absorption of the red, orange, and yellow end of the spectrum.

Litmus is a blue colour obtained from lichens, and very familiar to chemists as an indicator of acids. As a colouring agent of either foods or stuffs, it is of little importance, not being a "fast colour." Its spectrum is shown at Nos. 25 and 26.

§ 63. Brown Colours.—*Caramel.*—All shades of brown, from a rather delicate fawn colour up to black or nearly so, can be given by caramel. Caramel is not a single simple substance, but a mixture of various colouring-matters derived from the dehydration of sugar. Caramel is soluble in water, and is precipitated by alcohol.

Caramel, as it usually occurs, is almost all soluble in water, and gives precipitates with alcohol, ammoniacal lead acetate, and baryta water. It gives a spectrum without definite absorption-bands, but extinguishes the blue side of the spectrum, like ferric chloride. Caramel may be suspected in a brown liquid not coloured by a mineral substance, which is not decolourised when sufficient tannin is added, for the colouring-matter of berries is precipitated by tannin. Among the members of caramel, there are three principal substances—viz., caramelane, $C_{12}H_{28}O_9$, carameline, and caramelin.

Caramelane makes up the chief bulk of ordinary caramel. It is brown, hard, and brittle, bitter to the taste, without odour, deliquescent, and very soluble in water, sparingly soluble in weak alcohol, insoluble in ether. It does not precipitate metallic salts in aqueous solutions, but reduces an alkaline solution of oxide of copper, and also the salts of gold and silver.

Carameline may be separated from caramelane by first extracting the latter by alcohol of 84 per cent., exhausting with cold water, and precipitating with absolute alcohol. It is a brittle solid, of great tinctorial power; it is easily soluble in water, sparingly in alcohol, insoluble in ether.

Caramelin is a mixture of three substances of different solubilities; it is black, shining, and infusible. Its solutions precipitate metallic salts, and reduce gold and silver solutions.

§ 64. The following useful scheme may be followed in the detection of unknown colouring-matters. It is based on the scheme originally, in part, recommended by Professor Stein, in order to detect the dyes of various fabrics; but it is available, with the modifications introduced, when applied to the investigation of coloured foods, &c.:—

RED COLOURS.

A. Heat with Ammonium Sulphide.—A greenish or bluish colour, which, by the action of baryta water, is changed into green—**ALOES PURPLE.** If the liquid becomes purple, **ARCHIL** is also present.

B. Boil with a Solution of Aluminium Sulphate.

a. The liquid is coloured red, with a beetle-green reflection—**MADDER.** (Confirm by spectroscope.)

b. The liquid becomes red, but there is no reflection. Add an equal volume of sodium sulphite.

(1.) It is bleached. Presence of **BRAZIL-WOOD, SANTAL, MAGENTA, CORALLINE, SAFRANIN.**

Boil with Alcohol of 80 per cent.

a. The liquid colours distinctly. If bluish-red, **MAGENTA**; if yellowish-red, **SANTALIN.**

b. Liquid colours very little, or not at all—**BRAZIL-WOOD, CORALLINE, SAFFLOWER.**

(1.) Heat with lime water. No colour—**SAFFLOWER.** Red colour—**BRAZIL-WOOD, CORALLINE.**

(2.) Heat with dilute sulphuric acid. Orange colour—**BRAZIL-WOOD.** Yellow turning to grey on addition of copper chloride—**CORALLINE.** (Confirm by spectroscope.)

(2.) It is not bleached—**COCHINEAL LAC-DYE, LAC-DYE, KERMES, ARCHIL.**

(a.) Boil with alcohol; liquid becomes red—**ARCHIL.** If it only faintly colours, or at least if the colour is not decided, it may be **COCHINEAL, LAC-DYE, KERMES.**

(b.) Heat with baryta water; no change—**LAC-DYE**; the liquid becomes red—**COCHINEAL, KERMES.**

(c.) Heat with lime water: a red colour—**KERMES**; a violet colour—**COCHINEAL.**

YELLOWS.

Heat with a dilute solution of neutral ferric chloride.

N.B.—This test must be applied when the colouring-matter is separated in a fairly pure state.

A. Colour but little altered—**ANNATTO, TURMERIC, ANILINE YELLOW, PICRIC ACID, NAPHTHALINE YELLOW.** Test with a drop of concentrated sulphuric acid: a blue or green colour is produced—**ANNATTO.** If the spot becomes at once, or after a little time, more or less brown or red, then add alcohol, with a few drops of hydrochloric acid and some boric acid.

(a.) Liquid becomes of an intense pink colour, and on diluting with water, there is a reddish-yellow colour—**TURMERIC.**

(b.) Pale pink colour, on dilution with water, crimson—**ANILINE YELLOW.**

(*c*.) There is no change of colour on the addition of hydrochloric acid, &c. Heat with ammoniacal copper solution, *bluish-green;* confirm the presence of picric acid by the cyanide of potash test, a blood-red colour—**PICRIC ACID**; the colour becomes an olive green—**NAPHTHALINE YELLOW.**

B. Various shades of colour from green to almost black—**MADDER YELLOW, FUSTIC, FUSTET, QUERCITRON, FLAVIN, BERRIES, WELD.** Boil with aluminium sulphate, with the addition of an equal volume of water; liquid becomes yellow, with a red reflection—**MADDER YELLOW,** with tin. Yellow, with a bluish-green reflection—**FUSTIC.** Liquid yellow without reflection. Heat with baryta water, a red colour—**FUSTET.** The colour is only darkened. Boil with glacial acetic acid. On cooling, if the liquid is yellow, or greenish-yellow—**ENGLISH FLAVIN.** If the solution is not at all, or only faintly, coloured, boil with basic lead acetate. This, with regard to fabrics, if a tissue is *dyed* with **WELD,** the tissue will not change colour; if with **QUERCITRON** or **BERRIES,** the tissue will change to orange-brown; but articles of food will be scarcely coloured with these substances.

GREEN COLOURS.

If the green colouring-matter is not soluble in water, it is probably chlorophyll, unless indeed it is a mineral colouring substance. Chlorophyll best recognised by the spectroscopic characters of its alcoholic solution (see page 90). If not chlorophyll nor a mineral substance, then

A. Boil with a moderately concentrated solution of potassic cyanide.

(*a*.) Colour changes into brown or yellow—**ANILINE GREEN, GREEN,** containing **INDIGO-SULPHURIC ACID** (carmine green).

(*b*.) Does not change, or changes into a brownish- or yellowish-green—**GREEN,** containing **INDIGO** with or without **CARMINE GREEN**

B. In any of the foregoing cases add an equal volume of water, and then a solution of aluminium sulphate until an abundant precipitate is formed; filter and wash. (Excess of the precipitate must be avoided.)

(*a*.) Filtrate yellow or reddish—**ANILINE GREEN.**

(*b*.) Filtrate blue—(1) precipitate colourless—**CARMINE GREEN** with **PICRIC ACID**; (2) precipitate yellow—**CARMINE GREEN** with a vegetable yellow. Dissolve the yellow precipitate in water, add sulphuric acid, and filter: a green fluorescence—**FUSTIC**; no fluorescence—**WELD, TURMERIC.** Test for turmeric in the original substance by boiling with alcohol, and adding boric and hydrofluoric acids.

(*a*.) Filtrate colourless, precipitate yellow—**INDIGO.**

(*b*.) Filtrate blue; if the precipitate is colourless, **PICRIC ACID** may be present, and should be tested for; if coloured, there is probably a vegetable colour present.

BLUE COLOURS.

Dissolve out the colouring-matter with alcohol of 80 per cent., or treat the substance itself with alcohol, allowing it to remain in the liquid, and add a few drops of hydrochloric acid: a red colour—**LOGWOOD.** Confirm by adding to an alcoholic solution ammonia and then alum; a blue or violet precipitate should result. If the liquid does not dissolve any of the colour, it is most probably Prussian blue, but it may also be indigo. If, on the other hand, although some of the colour is extracted, yet the substance still remains blue, it is probably **ANILINE BLUE** or **INDIGO-SULPHURIC ACID.** Add strong sulphuric acid, with **INDIGO-SULPHURIC ACID,** no change. The colour changes into a yellow or reddish-brown in presence of **ANILINE BLUE.** On heating with sodium carbonate again, **INDIGO** is not changed, but **PRUSSIAN BLUE** is changed into yellow or brown.

VIOLET AND PURPLE COLOURS.

Heat with ammonium sulphide.

A. The tissue is bleached; soluble **ANILINE VIOLET, MAGENTA,** with **INDIGO CARMINE.** These two may be distinguished by the action of boiling alcohol: **SOLUBLE VIOLET** remains violet, **MAGENTA** becomes red, the substance becomes brownish-red.

Presence of **MAUVE,** or **HOFFMAN'S VIOLET.** These may be distinguished by the addition of hydrochloric acid, which colours **HOFFMANN'S VIOLET** yellow, but **MAUVE** becomes purple.

B. Turns olive brown—**ALKANET.** (Confirm by spectrum.)

D. Hardly any change. Presence of **ARCHIL, ARCHIL** with **INDIGO, LOGWOOD,** or **MADDER.**

Boil with alcohol—

a. The solution is pink, and changes to violet on the addition of ammonia **ARCHIL;** if the **ARCHIL** is accompanied with **INDIGO,** hot chloroform will colour blue.

b. Solution in alcohol remains colourless. Heat with dilute hydrochloric acid: **LOGWOOD** is coloured red, and may be further identified by test already given; if **INDIGO** is associated with it, hot chloroform will colour blue. With hydrochloric acid, madder, if it is coloured at all, becomes yellow.

The accompanying Tables will also be found useful in the identification of organic colours.

THE MINERAL MATTERS OR "ASH" OF FOOD.

ANALYSIS OF THE ASH OF ORGANIC SUBSTANCES.

§ 65. As a general rule, testing the ash for abnormal metals and alkaline earths is necessary, and more especially if the ash present any unusual character, whether in weight, colour, or

solubility. Leaving for the present the *special* tests, the number and nature of the constituents which require to be determined for the purpose of the food-analyst, vary according to the particular substance under examination, *e. g.*—

In all substances, *the percentage.*

In such fluids as milk, *the alkaline phosphates and the chlorides.*

In seeds, such as wheat, cocoa, &c., the total *phosphoric acid.*

In beer-ash, the amount of *common salt.*

In bread-ash, the presence or absence of *alumina, magnesia,* and proportion of *silica* to *alumina.*

In tea-ash, the *alkalinity*, the *iron*, the *silica*, and proportion of *soluble* to *insoluble ash.*

In coffee-ash, likewise the proportion of soluble to insoluble ash, but the presence or absence of *silica* becomes also of importance.

From these illustrations (which might be multiplied) it follows that, for the purposes of the food-analyst, the general constitution of the ash will be sufficiently known when the following determinations have been made :—

(1.) The total percentage of ash.
(2.) The total percentage of ash soluble in water.
(3.) The total percentage of ash soluble in acid.
(4.) The alkalinity of the ash.
(5.) The percentage of chlorine.
(6.) The percentage of phosphoric acid.

(1.) *The Total Percentage of Ash.*—Of the various methods of estimating an ash, the simplest and most practical appears to be —to place a sufficient quantity of the substance to be burnt in a capacious platinum dish, and to consume at the lowest possible temperature by heating with a ring burner.* The quantity to be taken is regulated by the amount of ash in the substances. For example, flour, containing only ·7 per cent. of ash, would give with 50 grms. ·35 ash, which is about as small a quantity as it is possible to work with conveniently, whilst in the case of coffee, tea, and cocoa, from 5 to 20 grms. is for most purposes ample.

* If the sulphuric acid in the ash is not to be determined, a wide glass tube (such as the chimney of a common paraffin lamp) adjusted over the dish, by its powerful up-draught greatly expedites the operation ; but if the sulphuric acid is to be determined, the impure gas of commerce renders the results too high. It is, however, of course open to the analyst to make the gas pass through a proper absorption-apparatus, or to use as a fuel, alcohol.

(2.) *The Soluble Ash.*—The ash is boiled up two or three times with water in the same platinum dish; filtered, and the filtrate evaporated to dryness, heated to dull redness, and weighed.

(3.) *The Ash Soluble in Acid.*—The portion of ash insoluble in water is boiled up with HCl, and filtered from the sand; the latter is washed, dried, and weighed.

(4.) *The Alkalinity of the Ash.*—The solution in water from (2) is coloured with cochineal, and titrated with d. n. acid: the result may be usually expressed as potash.

(5.) *The Percentage of Chlorine.*—The determination of chlorine in the ash usually gives results too low, especially if the substance burnt is one like bread, of difficult combustion, or containing substances which decompose chlorides at a red heat. Notwithstanding this defect, in a series of ashes burnt under similar circumstances, the amount of chlorine found gives fair comparative results. Should there be any special necessity for an accurate determination of chlorine, no volatilisation will occur in the combustion of most articles of food, if they are simply well carbonised and not burnt to a complete ash, and if the charcoal be finely powdered and extracted with plenty of boiling water. The chlorine may be determined gravimetrically by nitrate of silver, or more conveniently by a standard solution of nitrate of silver, using as an indicator neutral chromate of potash. Should alkaline phosphates be present, they must be first removed by baryta water.

(6.) *The Phosphoric Acid.*—The usual method of determining phosphoric acid is to dissolve the ash in hydrochloric acid, evaporate to dryness, remove the silica, mix the acid filtrate with ammonia in excess, redissolve the precipitated earthy phosphates by acetic acid, filter off and estimate the insoluble phosphate of iron (and alumina, if present), precipitate the lime with oxalate of ammonia, and then in the fluid (free from lime and iron) precipitate the phosphoric acid, by the addition of ammonia and magnesia mixture.

§ 66. *General Method of Determining all the Constituents of an Ash.*—The best method of determining *all the constituents* of an ordinary ash is perhaps as follows:—A sufficient quantity of the ash (from 5 to 10 grms.) is placed in a flask, about 25 cc. of water added, and saturated with CO_2; the liquid is now evaporated to dryness, heated with a small quantity of water to dissolve the alkaline salts—the solution is filtered through a small weighed filter, the filtrate evaporated to dryness, the saline residue treated with a small quantity of water, and the calcium sulphate which separates out filtered through a weighed filter, and estimated; the filtrate from this is put in a tared flask,

made up to any convenient weight, and divided into five portions *by weight*, viz.—

(1.) For CO_2.—This is most accurately determined by the use of the following little apparatus:—The solution is placed in a flask A, and sufficient acid is put into the short test-tube T, to more than neutralise the carbonate. A stout glass rod is passed through the doubly perforated caoutchouc cork, and supports the little tube in position. The carbonate solution is now boiled until steam hisses out of the tube G (which it is convenient to furnish with a Bunsen's valve*). G is then placed under the mouth of a graduated measuring tube filled with mercury, and it is at once seen whether all the air is expelled. The flame is withdrawn for a second, and the glass rod, which moves quite airtight, is pulled a little up, so as to allow the acid tube to fall down and empty its contents into the alkaline fluid. The flame is again placed under the flask, and the CO_2 boiled out into the measuring apparatus, and measured in the ordinary way. Those who are not provided with gas apparatus will find it convenient to jacket their eudiometer with a tube open at both ends. The lower end is closed by the mercury in the bath; the upper is placed under a water-tap, and a syphon is adjusted so as to prevent overflow. In this way the gas is rapidly cooled, and the whole determination, from first to last, need not take more than a quarter of an hour.† Instead of boiling the solution in this way, those who possess the mercury pump described and figured at page 70 (fig. 7), will find it more convenient to make the flask vacuous, then upset the acid, and collect the gases expelled.

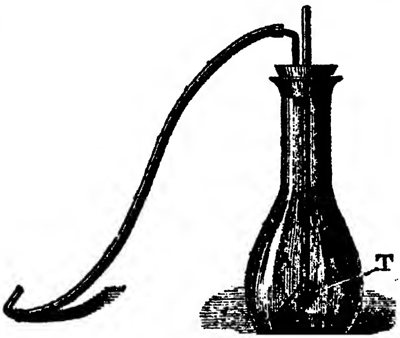

Fig. 13.

* Bunsen's valve is made as follows: Take a piece of rather thick-walled india-rubber tubing, say, three inches in length; work it, by the aid of a little spirit, on to any wooden rod which is of sufficient size to stretch it well; then with a sharp chisel, by a single blow, cut a longitudinal slit; if well made, it allows air to go one way with the greatest ease, but effectually prevents a return.

† Much ingenuity has been expended on the estimation of carbon dioxide, and the old method of estimating in light glass apparatus, by the loss of weight, is quite forsaken. The method given in the former edition of this work was to absorb the CO_2 in a clear solution of ammoniacal calcium chloride, collect the precipitated calcium carbonate, and titrate it with d. n. acid,

(2.) For the sulphuric acid, determined by chloride of barium.

(3.) For the phosphoric acid, determined as magnesian pyrophosphate.

(4.) For the chlorine, by precipitation as silver chloride.

(5.) For the alkalies, by boiling in a platinum dish with slight excess of baryta water, filtering, getting rid of the excess of baryta by ammonia and ammonium carbonate, evaporating the filtrate to dryness, converting the alkalies into chlorides, and determining their relative proportion from their total weight and their content in chlorine. This completes the analysis of the *soluble* portion of the ash.

The *insoluble* will contain lime, magnesia, ferric oxide, alumina if present, silica, phosphoric, sulphuric, and carbonic acids.

The main portion of the insoluble ash is dissolved in nitric acid, freed from silica in the usual way, evaporated again to dryness in a porcelain basin, dilute nitric acid added until the bases are completely dissolved, and strong fuming nitric acid added, until the solution begins to be turbid from the separation of calcic nitrate. The turbidity is now destroyed by a few drops of dilute nitric acid, the solution warmed, and tinfoil added in small portions at a time, in weight about equal to the amount of ash taken. When the tin is fully oxidised, the solution is evaporated *nearly* to dryness, water is added, and the solution filtered; the phosphoric acid is retained in the precipitate—the bases are all in the filtrate. The precipitate is dissolved in strong potash solution, acidified with sulphuric acid, and freed from tin by hydric sulphide, concentrated to a small bulk, filtered if any further sulphide of tin separates, and the phosphoric acid determined by magnesia mixture and ammonia.*

The filtrate from the tin phosphate must be freed from lead (if the tin originally contained lead) by hydric sulphide, concentrated, the iron and alumina separated and determined by ammonia, the manganese separated as binoxide by brominewater, the lime by oxalate of ammonia as oxalate, and the magnesia determined in the usual way as pyrophosphate.

A weighed portion of the insoluble ash must also be taken for the carbon dioxide, sulphuric acid, and sand. The carbon dioxide is determined in the manner already described.

using as an indicator cochineal. Another method which has been proposed, is to make a combustion of the substance with potassic bichromate, and absorb the CO_2 in the usual way in potash bulbs. A third, is to let the acid drop from a separating funnel on to the carbonates, and absorb the CO_2 as in the last, an aspirator and drying tubes being used. (*Annalen der chemie*, clxxvi. 136-144.) All of these methods, in the author's opinion, are inferior to that given above in the text.

* Thorpe's "Quantitative Analysis." Lond., 1877.

The process just given is not quite accurate with regard to the estimation of the alkalies; for Bunge * has shown that since the alkalies form insoluble compounds with the alkaline earths, a watery extract of the ash gives low results. For example, Bunge incinerated 300 cc. of cow's milk; from a watery extract of the ash he obtained

$$K_2O \cdot 5436, Na_2O \cdot 0700;$$

while from a subsequent nitric acid extract of the same ash,

$$K_2O \cdot 0937, Na_2O \ 0 \cdot 1162.$$

If chlorides of the alkalies be heated with tribasic phosphate of lime, the soda is specially likely to combine with the lime in insoluble combination—in far less proportion the potash.

Bunge recommends the following method:—The watery extract is decomposed with baryta water until a film forms on the surface of the solution, the mixture is warmed and filtered hot. The excess of baryta is got rid of by CO_2, subsequent warming, and filtration; the filtrate is evaporated in a platinum dish, the residue gently ignited, dissolved in a little water, filtered through a small filter, and evaporated with HCl in a small platinum dish. The chlorides are then ignited, weighed, and separated by platin chloride.

The hydrochloric or nitric solution of the insoluble portion of the ash is evaporated to dryness in a platinum dish, the residue again dissolved in a little of the acid and water, treated like the former with baryta water, and filtered hot. Ammonia and carbonate of ammonia are now added, the liquid filtered, and the filtrate evaporated in a platinum dish, and ignited at the lowest possible temperature. The residue still containing a trace of alkaline earth, is extracted with water, evaporated with oxalic acid, ignited again, taken up with water, filtered, evaporated in a small platinum dish, ignited again, dissolved in a little water, and lastly, evaporated with HCl, and the alkaline salts separated by bichloride of platinum.

Since a determination of the ash only gives those mineral substances which are fixed in the fire, and destroys nitrates, and changes oxalates, citrates, and tartrates into carbonates, while other constituents, under the influence of heat, undergo a new arrangement, it becomes a question whether the ingenious method recommended by E. Laugier † in the analysis of sugar, would not be applicable in several cases.

* Liebig's *Annalen der Chimie u. Pharmacie.*
† *Compt. rend.*, lxxxvii. 1088–1090.

M. Laugier takes two portions of sugar, one for the ash, the other for the organic acids, the latter being exactly double the quantity of the former. To the larger quantity of the sample, dilute sulphuric acid is added drop by drop to set free the organic acids; the acidified sugar is mixed with pumice stone and exhausted with ether; half of the ethereal solution is added to the ash obtained from the smaller portion, and evaporated down upon it and weighed. By this means M. Laugier thinks that he reconstructs the original salts in the sugar. This, however, cannot be entirely true. The other half of the ether solution is titrated with an alkali.

PART III.—CARBO-HYDRATES.

STARCHY AND SACCHARINE SUBSTANCES.

SUGAR.

§ 67. Sugars may be divided into two classes:—(1.) Those capable of being broken up by the process of fermentation, such as the sugars known as the glucoses and saccharoses; and, (2.) the unfermentable sugars, to which class belong many sweet principles found in plants, such as eucalyn, sorbite, quercitose, inosite, mannite, dulcite, &c. The important sugars to the food-analyst are, cane sugar or saccharose, glucose or dextrose, levulose, milk sugar,* and maltose.†

Cane Sugar, $C_{12}H_{22}O_{11}$, occurs in a very large number of plants, but is only manufactured from beet-root, the sugar-cane, sorghum, and the sugar-maple. Its specific rotatory power is $+73·8$. It crystallises from its solutions in water or dilute alcohol in anhydrous crystals, the specific gravity of which is 1·606. It is soluble in one-third of its weight of cold water, and is very soluble in hot; in absolute alcohol it is insoluble, the solubility rising in proportion to the weakness of the alcohol. Thus, according to Scheibler, the numbers in Table IV. are the percentages of sugar dissolved, and the specific gravity of the solution at the common temperature of 14°.

When solutions of sugar are boiled with dilute mineral acids, the sugar is split up into two glucoses: the one rotating to the right, hence named dextrose, the other rotating the plane of polarised light, to the left—levulose.‡ Long boiling with water has, to a slight degree, the same effect, and it is also shown in the action of ferments, when exposed to light. An uncorked solution of sugar (or one imperfectly sealed) will in a few days, according to the temperature, show some degree of inversion. But a boiled solution of sugar, which, while actually boiling, has been her-

* Milk-sugar is fully described in the article on "Milk."

† "Maltose" is described in the article on Malt Liquors.

‡ To this mixture of dextrose and levulose, the term "*invert* sugar" is applied, because the polarisation is the opposite of that of cane sugar; for although glucose rotates to the right and levulose to the left, yet the latter is so much stronger that the solution polarises to the left.

TABLE IV.—SOLUBILITY OF SUGAR IN ALCOHOL OF DIFFERENT STRENGTHS.

Per cent. alcohol.	100 cc. of the solution contain	Specific gravity of the saturated solution.
0	85·8	1·3248
5	82·4	...
10	79·4	1·2991
15	76·5	...
20	73·4	1·236
25	69·8	...
30	66·0	1·2293
35	61·6	..
40	56·7	1·1823
45	51·6	...
50	45·7	1·1294
55	39·6	...
60	32·9	1·050
65	25·6	...
70	17·8	0·9721
75	11·2	...
80	6·4	0·8931
85	2·7	...
90	0·7	0·8369
95	0·2	...
97·4	0·08	...
100	000	...

metically sealed, will keep unchanged for years. Acetic acids, and the vegetable acids generally, have little or no effect in the "inverting" of sugar.

Carbon dioxide, especially under pressure, inverts sugar.* Pure cane sugar, if free from glucose, undergoes no change of colour when boiled with the alkalies; if, however, glucose be present, there is a very decided change.

Sugar forms a few well established compounds with bases, and many with salts. The most definite of the sugar compounds combined with bases are those which it forms with baryta and lime. If a solution of sugar be boiled down with sulphide of barium or baryta, a sandy precipitate forms, having the composition $C_{12}H_{22}O_{11}BaO$; and on decomposition of this with CO_2, pure sugar is obtained. A commercial process based upon this reaction is in use in order to recover the sugar from molasses, and it may be employed in certain cases in the laboratory with advantage.

There is a monobasic lime sucrate ($C_{12}H_{22}O_{11}CaO$) corresponding to the barium compound, and a tribasic sucrate of lime ($C_{12}H_{22}O_{11}3CaO$). Crystalline compounds are also easily obtained with certain sodium salts; thus, there is a chloride of sodium

* V. Lippmann, *Ding. Poly. J.*, ccxxxvij. 146-163

compound $C_{12}H_{22}O_{11}NaCl.2H_2O$; and another having the formula, $2C_{12}H_{22}O_{11}3NaCl.4H_2O$. An iodide of sodium compound may be obtained in large crystals having the following composition: $2C_{12}H_{22}O_{11}3NaI.H_2O$.

Sugar heated to 160° melts to a colourless liquid; on cooling the melted mass is at first clear and transparent, but in a little time it becomes crystalline and opaque. At about 170° to 180° it loses water, and is said to be transformed into dextrose and levulosan; as the heat is increased, water is continually being lost, and more or less brown products are formed (see "Caramel," p. 93). If sugar is fused with zinc chloride, a liquid is obtained which yields, on distillation, aldehyde, acetone, metacetone, formic acid, acetic acid, furfurol, and apparently mesityl oxide; carbon dioxide, carbon oxide, and hydrocarbons are also formed; and there is also a sublimation of crystals, hexmethylbenzene, $C_6(CH_3)_6$. (*Lippmann.*)

Bromine, according to E. Reichardt, transforms one-third of cane sugar into gluconic acid, one-third into glucose, and the remainder into gum.

§ 68. *Adulterations of Sugar.*—Loaf sugar is, as a rule, chemically pure. It is probably, indeed, the purest food-substance in commerce, and a large quantity may be burnt up without obtaining a trace of nitrogen, and without leaving any residue. The only sugars that may be impure are the "raw" sugars.

The adulterations of sugar usually enumerated are: Glucose or starch sugar, sugar of milk, dextrine, chalk, plaster, sand, and various species of flour. No conviction, that the author is aware of, under the Sale of Food and Drugs Act, has been hitherto obtained in England for selling sugar which had been adulterated; and the impurities given above are not according to the author's experience, but rather the stereotyped list enumerated by various authors in different countries, representing more what is possible, than what actually exists.

To detect glucose (dextrose) in the presence of other sugars, B. Bottger* mixes the solution with an equal quantity of carbonate of soda solution [1 of the salt to 3 of water], and then adds a little basic bismuth nitrate, boils, noticing whether there is any blackening, which is taken as an indication of dextrose.

E. Brucke† has modified this method, so as to eliminate any blackening (which might occur from the sulphur in albuminous matters), by using potassium bismuth nitrate, which precipitates albumen. The re-agent is made by dissolving basic bismuth

* *Jour. für. Prakt. Chem*, lxx. 432.
† *Wien Akad. Ber.*, 1875, 52.

nitrate in a hot solution of potassic iodide with the addition of hydrochloric acid. The albumen precipitated by the re-agent is of course filtered off, and the filtrate is boiled.

The simplest and best method, however, of detecting starch sugar when mixed mechanically with cane sugar, is undoubtedly that recommended by P. Casamajor.* The suspected sugar is thoroughly dried, and is then treated with methyl-alcohol which has been saturated with starch sugar. 100 cc. of methylic alcohol of 50° strength dissolves about 57 grms. of starch sugar, the 100 cc. becoming in volume 133 cc. Such a saturated solution dissolves cane sugar readily enough, but leaves starch sugar undissolved. After stirring the sugar in the methylic alcohol for about two minutes, the residue is allowed to settle, and the clear solution decanted. The residue is now washed with the same solution, and after stirring and allowing the residue to settle again, if starch sugar were present there will remain a certain quantity of chalky white specks, accompanied by a fine deposit of starch sugar. By collecting this on a filter, and washing rapidly with nearly absolute methyl, approximate quantitative results may be obtained.

The best method of detecting dextrine when mixed with sugar, has been specially studied by Scheibler.† He took a sugar which gave the following numbers to analysis :—

	Per cent.
Water,	3·35
Ash,	1·73
Organic matter,	2·32
Sugar,	92·60

and mixed this sugar with various proportions of dextrine—from 1 to 3 per cent.—and examined the behaviour of the sugar, both optically and chemically. The polarisation indicated the following amounts of cane sugar :—

0·9	0·5	1·0	2·0	3·0	per cent. dextrine.
92·6	93·4	94·0	95·6	96·3	,, sugar.

Thus, a sugar adulterated with 3 per cent., if examined optically, would indicate 96·3 per cent. of cane sugar instead of 92·6. On inverting the sugar, there were great discrepancies, quite enough to make even an inexperienced observer suspect something wrong. Thus with the same amounts of dextrine, the pure sugar

* *Chemical News*, 1880.

† "The Sugar Cane." 1871, p. 469.

showing, before inversion, 92·6 per cent. of sugar, and after inversion, 92·5 :—

	0·5	1·9	2·9	3·0	per cent. dextrine.
Direct,	93·4	94·2	95·6	96·3	,, sugar.
After inversion,	80·4	78·0	73·1	67·0	,, ,,

It was no use to experiment beyond 3 per cent., because it was then impossible to clarify the solution by lead acetate sufficiently for the purposes of optical analysis. Scheibler summarised his results as follows : Dextrine may be detected by its thus raising the degree of rotation, by the great difference of the results before and after inversion, by the blue colour it gives with iodine (although there are dextrines which, when added to sugar, may show this test imperfectly), by the impossibility of clarifying the liquid should any amount be present, by lead acetate, and lastly, by partial separation of the dextrine by animal charcoal.

Insoluble mineral matters, such as sand, present in low-class sugars as an impurity, may be readily detected by simple solution of the sugar and filtration. Gummy matters may also be separated by precipitation by alcohol in the way to be described in the article on "Tea;" mineral matters, generally, may be detected in the ash. Beet sugars, and to a less degree cane sugars, will contain a large amount of potassic and sodic carbonates, arising from the decomposition of the citrates, malates, oxalates, &c. Beet sugars may also contain nitrates. Cane sugar leaves an ash containing but little soda, with much more lime, magnesia, iron, and alumina. Thus, the following is the ash of raw cane and beet sugars, obtained in the following manner: All the mineral matters in the sulphuric acid residue of a large sugar factory were kept for a whole year, and analysed at the end of the year. Of course the carbonates, nitrates, and chlorides have all been decomposed, and the analysis is true only with regard to the bases.

	Cane Sugar Ash. Per cent.	Beet Sugar Ash. Per cent.
Potash,	28·79	34·19
Soda,	·87	11·12
Lime,	8·83	3·60
Magnesia,	2·73	·16
Oxides of iron and aluminium,	6·90	·28
Sulphuric acid [anhyd.],	43·65	48·85*

Dividing each factor of the ash of the beet sugar by that of the cane, we get the following proportions for the bases:—

* J. Wallace, *Chem. News*, xxxvij. 75.

	Cane.	Beet.
Potash,	1	1·19
Soda,	1	12·78
Lime,	1	·41
Magnesia,	1	·06
Oxides of iron and aluminium,	1	·04

In other words, the potash is almost equal in the two ashes, but there is nearly thirteen times more soda in beet ash than in cane sugar ash; lime, magnesia, and oxides of iron and aluminium, are in very small quantities in beet sugar ash.

An analysis of the ash of a Demerara cane sugar growing near the sea-coast, by Dr. Wallace, is as follows:—

	Per cent.
Potash,	29·10
Soda,	1·94
Lime,	15·10
Magnesia,	3·76
Sulphuric anhydride,	23·75
Phosphoric acid,	5·59
Chlorine,	4·15
Carbon dioxide,	4·06
Iron peroxide,	·55
Alumina,	·65
Silica,	12·38
	101·03
Deduct oxygen = chlorine,	·93
	100·10

If sugar be ever adulterated by any of the starches, so clumsy a fraud is readily detected by a microscopical examination, and the use of iodine to the residue obtained by dissolving the sugar in cold water, and then filtering.

§ 69. *Full Analysis of Sugar.*—The full analysis of a raw sugar consists in:—

1. Determination of the water driven off at a heat not exceeding 55° to 60°.
2. An optical estimation before and after inversion.
3. Titration with copper oxide before and after inversion.
4. Estimation of the organic acids by treating with sulphuric acid, and shaking up this acid extract in the tube figured at page 69 with ether, until it has dissolved out all the organic acids.
5. Titration of the organic acids with d. n. soda or potash.
6. Estimation of any insoluble matter, whether organic or inorganic.
7. Estimation of the ash and its constituents.

It may also be necessary to estimate the matters precipitated by basic lead acetate; it would be, however, quite sufficient for commercial, and, indeed, for most purposes, to merely estimate the percentage of cane sugar, fruit sugar (if present), water, and organic matter, or water and ash, as in the following analyses :—

TABLE V.—COMPOSITION OF RAW BEET-ROOT SUGARS OF GOOD QUALITY.

	Cane Sugars. Per cent.	Organic Matter. Per cent.	Water. Per cent.
1. Clear light mixed product, ...	85·0	1·6	2·0
2. Light mixed product, ...	93·0	2·0	2·3
3. Half white, 1st product, . . .	94·3	2·3	2·5
4. Light mixed product, ...	93·5	2·4	3·3
5. ,, ,, ,, ...	94·4	3·1	2·2
6. Half white, 1st product, . . .	96·1	2·3	3·4
7. Clear white, 1st product, . . .	92·0	3·7	2·8
8. Light mixed, 1st product, . . .	93·5	3·0	2·8
9. Clear light mixed, 1st product, . .	92·0	2·3	2·6
10. Clear light, 1st product, . . .	93·1	3·3	3·0
11. Clear light, 1st product, . . .	94·0	3·0	2·9
12. Clear yellow mixed product, . .	92·0	3·0	2·3
13. Yellow mixed product, . . .	92·0	2·4	3·5
14. Clear yellow mixed product, . .	92·0	3·2	3·1
15. Clear yellow, 1st product, . . .	93·7	2·6	2·8
16. Yellowish mixed product, . . .	91·8	2·9	3·6
17. Yellow mixed product, . . .	93·0	3·5	2·7
18. ,, ,, ,, ...	93·4	2·9	2·3
19. ,, ,, ,, ...	93·0	2·3	2·9
20. Yellowish ,, ...	93·0	3·7	3·1
21. Yellow mixed product, . . .	93·0	3·3	2·7
22. Light mixed product, ...	91·6	3·0	3·0
23. Yellow ,, ,, ...	90·7	4·6	4·3
24. ,, ,, ,, ...	93·8	2·1	2·8
25. ,, ,, ,, ...	92·5	2·4	3·5
26. Yellowish mixed product, . . .	90·0	4·3	3·7
27. Yellowish brown, 2nd product, . .	91·3	5·1	2·5
28. Yellow, 1st product, ...	92·4	3·5	2·6
29. Yellow mixed, 1st product, . . .	89·5	4·0	3·7
30. Light yellow, 1st product, . . .	92·0	2·8	3·4
31. Yellow mixed product, . . .	89·6	4·3	3·8
32. Brownish, 2nd product, . . .	89·0	6·3	3·0
33. Second product, ...	87·0	6·2	4·1

TABLE VI.—SOME ANALYSES BY MR. HALSE OF CONCRETES.

	Cane Sugar. Per cent.	Uncrystallised Sugar. Per cent.	Water. Per cent.	Ash. Per cent.
1.	87·20	4·00	4·50	1·38
2.	89·60	1·90	5·50	·85
3.	90·20	1·95	4·03	·99
4.	91·70	3·30	2·15	·88
5.	87·00	5·00	4·72	1·24
6.	95·10	1·40	1·56	·86
7.	94·30	1·70	2·21	1·16
8.	92·50	1·92	2·70	1·18

The difference between the totals and 100 would be returned as "unestimated matters and loss."

The methods of estimating the different kinds of sugar are fully considered in the next section, and it only remains to detail the best methods of taking the ash of a sugar.

There are two methods of taking the ash of sugar.

The one is simply to burn the ash in the ordinary way in a platinum dish heated to redness in a current of air. In the case of all substances like sugar or starch, this method is very tedious, and without doubt there is some loss by volatilisation. Landolt* determined the amount of this volatilisation by a series of careful experiments, and gives the following Table (VII.), which may be used as a guide to the correction of the final weight of the ash.

A method recommended and practised by Scheibler was to moisten the ash with sulphuric acid, whereby the combustion is much hastened, and the bases, being obtained as sulphates, approximate more nearly in weight to that of the organic salts naturally in the sugar, which in the other method are obtained as carbonates. It has also been proposed to precipitate the sugar with acetate of lead, and thus obtain the lead salts of the organic acids. The lead compounds are decomposed in the usual way, and the acids set free titrated by potash. The potash

* Landolt, H., *Journ. Für Praktische Chem.*, ciii. Also, "Sugar Cane," 1873.

combination approximates somewhat more closely to the actual salts of the sugar.

TABLE VII.

Weight of Residue.	Loss by Heating after			
	Half an Hour	One Hour.	One and a Half Hours.	Two Hours.
·01 grm.	·002 grm.	·004 grm.	·006 grm.	·008 grm.
·02 ,,	·002 ,,	·004 ,,	·007 ,,	·008 ,,
·03 ,,	·002 ,,	·005 ,,	·008 ,,	·010 ,,
·04 ,,	·003 ,,	·006 ,,	·009 ,,	·012 ,,
·05 ,,	·004 ,,	·007 ,,	·011 ,,	·015 ,,
·06 ,,	·004 ,,	·008 ,,	·013 ,,	·017 ,,
·07 ,,	·005 ,,	·010 ,,	·015 ,,	·019 ,,
·08 ,,	·005 ,,	·010 ,,	·016 ,,	·020 ,,

But the best of those methods which attempt to reconstruct from the ash the original salts, is probably that of Laugier, already described at p. 102. Laugier extracts the organic acids by ether, and then adds them to the ash, and evaporates them down with it. As to raw beet sugar ash, the experiments of Landolt appear to show that simply multiplying the potassic carbonate found by 2, gives the amount of organic salt from which it was derived.* His experiment was as follows:—Two pounds of syrup were fully precipitated by lead acetate, then decomposed by SH_2, and exactly neutralised by potash. The solution was next partly evaporated, passed through animal charcoal, and dried. It gave the reactions of chlorine, and of oxalic, malic, and tartaric acids, with a trace of sulphuric acid. Three separate portions were now carbonised, and the proportion for every one part of organic salt of carbonate of potash was—in experiment 1, 2·04; in experiment 2, 2·05; in experiment 3, 1·98: the mean of the three being 2·08.

§ 70. *Glucose, Dextrose, Dextro-glucose, Grape Sugar,* $C_6H_{12}O_6H_2O$—The rotatory power of glucose is 56°. It is soluble in 100 parts of cold water, and very soluble in boiling water; it is

* Or if Scheibler's process be followed, the alkaline sulphates may be multiplied by 1·54.

soluble in glycerine, in about two parts of rectified spirit, and two of amylic alcohol; but it is insoluble in ether and in chloroform. Dextrose is widely spread in the vegetable kingdom, but is never found unaccompanied by levulose. Dextrose is artificially obtained by heating carbo-hydrates, such as starch or cane sugar, with acids; in such cases, it is accompanied by dextrine, from which it is difficult to purify it. According to Hoppe-Seyler, indeed, it cannot be obtained pure, save from diabetic urine, and the specific rotation usually given is erroneous. He has separated pure grape sugar, dextrine free, from diabetic urine, and gives its polarisation as 53°·5. This, however, agrees very nearly with that given by Tollens, who ascribes to anhydrous dextro-glucose a specific rotation of 53°·1, and to the dextrose with its water of crystallisation a specific polarisation of 48°·27.

The best way to obtain dextrose from cane sugar in a pure state is, according to Soxhlet, the following:—3 litres of 90 per. cent. alcohol and 120 cc. of concentrated hydrochloric acid are made to act at 45° C. for two hours on 1 kilo. of cane sugar. After ten days, crystals of dextrose form, when the liquid may be concentrated by distillation, and the crystals which have formed removed. In a few days, the whole of the dextrose will have been deposited as a white powder. The crystals are washed with 90 per. cent. alcohol and with absolute alcohol, and crystallised out of the purest methyl-alcohol. Crystallised grape sugar is in the form of little masses of six-sided tables, which melt at 86°, and lose at 100° their water of crystallisation.

§ 71. *Levulose* (or *Levuglucose*) is isomeric with dextrose, but distinguished from it by its action on a ray of polarised light—turning to the left, instead of to the right: $-106°$ at 14°, $-53°$ at 90°. It is obtained in company with dextrose when sugar is "inverted" by the action of a dilute acid. To isolate levulose the acid must be got rid of; for example, if hydrochloric acid has been used, it is precipitated by silver solution: if sulphuric, by baryta water, &c. The solution of invert sugar must be about 10 per. cent. strength. To every 100 cc. 6 grms. of freshly burnt lime must be added, and the whole shaken. By artificially cooling the solution with ice, a crystalline magma is obtained, and by filtration the more soluble dextrose lime-compound can be obtained from the less soluble levulose lime-compound. The sugar thus obtained can be freed from lime by carbon dioxide.

Levulose is uncrystallisable, but in has not been found possible to separate it entirely from the crystalline glucose, by crystallising the latter out of it. It presents when pure simply the characters of a colourless syrup.

ESTIMATION OF SUGAR.

§ 72. Sugar is estimated by chemical processes, by the specific gravity of the solution, by the estimation of the CO_2 evolved in alcoholic fermentation, and by certain physical processes.

It is only possible to estimate percentages of sugar (especially cane sugar) from the specific gravity of the solution when the fairly pure sugar is dissolved in pure water, so that this method is of but limited utility, and seldom employed by the analyst. The fermentation process is too tedious and inconvenient ever to come into general practice, and will therefore not be described.

(1.) *Chemical Processes depending upon the Precipitation of the Suboxide of Copper from a Copper Solution by Grape Sugar.*

The most general of the numerous processes under this head is that of Fehling, which requires a solution of cupric sulphate and Rochelle salt, alkalised by soda. 34·64 grms. of pure crystallised cupric sulphate, previously powdered and pressed between blotting-paper, are dissolved in 200 cc. of distilled water; 174 grms. of Rochelle salt are dissolved in 400 cc. of a solution of pure caustic soda, specific gravity 1·14; the two solutions are now mixed and made up to 1 litre. The liquid should be preserved in bottles protected from the light, and absorption of carbon dioxide from the air should be provided against.

On account of the slight instability of this solution, A. Soldaini has proposed the following:—416 grms. of potassium bicarbonate, 15 grms. of dry basic cupric carbonate, and 1400 grms. of distilled water are heated together, the liquid being continually replaced; when the evolution of CO_2 has nearly ceased, the liquid is made up to its original volume with water, filtered, and concentrated down to 800 cc. Such a solution is not reduced by light or the carbon dioxide of the air: it is unaltered by prolonged boiling, and may even be evaporated to dryness without decomposition. It is reduced by formic acid, levulose, glucose, and lactose, and can be used for quantitative purposes in the same way as "Fehling."

Cane sugar cannot be estimated directly by "Fehling," since it does not reduce copper solution; by boiling with dilute acid it is, however, changed to inverted sugar, which reduces copper or mercury in exactly the same proportion as glucose.

Starch and starchy substances may be also changed into sugar by boiling for several hours with a dilute acid. The following is a convenient method:—Two or three strong assay flasks are

taken, and in each is placed from ·5 to 1 grm. of the substance to be examined, with 50 to 60 cc. of decinormal sulphuric acid; the flasks are stoppered with caoutchouc corks, tied down with strong string, and capped with linen or canvas, and the whole suspended in a water-bath and heated for from six to eight hours. At the end of four hours one of the flasks may be taken out, cooled, opened, and titrated; and at the end of six hours the second. If there is no marked increase in the amount of sugar between the first and the second, the operation is finished; but in any other case the third flask should be heated for another four hours before being examined. 100 parts of grape sugar = 90 of starch.

(2.) *Volumetric Processes by the aid of Solutions of certain Salts of Mercury.*

Knapp's mercuric cyanide solution is made by dissolving 10 grms. of mercuric cyanide in about 600 cc. of water, then adding 100 cc. of caustic soda solution of specific gravity 1·145, and diluting to 1 litre. 40 cc. of the mercury solution are placed in a flask, heated to boiling, and the solution containing sugar run in gradually from a burette, four parts of mercuric cyanide being reduced to metallic mercury for every one part of anhydrous grape sugar (or, 3·174 parts of metallic mercury = 1 anhydrous grape sugar). The ending of the process is discovered by moistening filter-paper with the clear solution, and holding quite close to it a rod dipped in ammonium sulphide solution; a *decided* brown coloration takes place if the mercury salt is in excess; but if the colour is very faint, the operation is finished, for it appears to be impossible to decompose the whole salt, a trace always remaining, and for this reason the solution should be standardised with sugar.

A. Sacchse uses the following solution for the estimation of sugar:—18 grms. of pure dry mercuric iodide, and 25 grms. of potassic iodide are dissolved in water, a solution of 80 grms. of caustic potash is added, and the whole made up to 1 litre. 40 cc. of this solution [$=0·72$ grm. HgI_2] are boiled in a basin, and the solution of grape sugar is run in, until the whole of the mercury is precipitated. The final point is determined by spotting a drop of the supernatant liquid on a white slab, and there bringing it into contact with a drop of a strongly alkaline solution of stannous chloride. The production of a brown colour shows the presence of unprecipitated mercury.

§ 73. Some recent researches of F. Soxhlet* bear upon the behaviour of the different kinds of sugar with the solutions just described. These experiments are of the more importance since they were made with the most scrupulous care, and with the purest materials, while the testing was done under varied conditions.

Invert Sugar.—Pure invert sugar he prepared by dissolving cane sugar which had been purified by thrice crystallising out of water, and dried at 50° in a vacuum over calcic chloride. 9·5 grms. were dissolved in 700 cc. of boiling water, to which had been added 100 cc. of hydrochloric acid, containing ·72 of HCl, and heated in the water-bath for half an hour. The liquid was finally neutralised with soda, and diluted to one or two litres as might be required. He found that invert sugar reduced Fehling's solution almost at once, and that in all cases two minutes were sufficient, no advantage being gained from a longer boiling; nor did it appear to matter whether the sugar was added to the liquid cold, and then boiled up, or the sugar added to the boiling liquid.

Soxhlet drew from this experiment the following conclusions:—

1. The proportion in which invert sugar reduces copper oxide is essentially influenced by the concentration of the liquid. Dilution of the copper and sugar solution lowers, excess of copper raises, the reducing power. ·5 grm. invert sugar in 1 per cent. solution corresponds to 101·2 cc. of undiluted Fehling's solution; but, if Fehling is diluted with four times its volume of water, then the same amount of invert sugar is equivalent to 97·0 cc. of Fehling: in the one case the proportion in equivalents being as 1 : 10·12, in the other as 1 : 9·70.

2. In the titration of an invert sugar solution, the first cc. of the sugar solution flowing into the copper reduces more copper than the next, and the last cc. has the smallest reducing power, because the first has the greatest excess of copper solution to act upon, and the last the smallest. It hence follows that the reduction proportion is not constant throughout the operation, but is continually falling, and that the values are purely empirical, and only correct by operating always with the same concentration of copper and sugar solution.

3. The accepted view that 1 equivalent of invert sugar reduces 10 of CuO is wrong. ·5 of invert sugar does not reduce 100 cc. of Fehling's solution diluted with 4 of water; 97 or 100 cc. of Fehling are not equivalent to ·500 grm., but to ·515.

Milk-Sugar.—Similarly with regard to milk-sugar, he gives

* *Journal f. Prakt. Chemie*, N.F. xxi., 227, 317; *Zeitschrift. f. Analyt. Chemie*, xx. 425.

the reduction proportion in equivalents as 1 is to 7·40, or ·5 grm. of milk-sugar in 1 per cent. solution is equal to 74 cc. of Fehling's solution. Dilution of the solution, or concentration, has a similar action to that of invert sugar, but smaller in degree. (See article on "Milk.")

Galactose.—Galactose reduces Fehling as quickly as invert or grape sugar. ·5 of galactose is equivalent to 98 cc. of undiluted Fehling. If the latter be diluted with four times its volume of water, then it corresponds to 94 cc. The reduction ratio in equivalents is as 1 : 9·8, and as 1 : 9·4 in the respective cases mentioned.

Maltose.—The behaviour of maltose, according to Soxhlet, is as follows:—

Maltose has the smallest reducing power of all the sugars. It reduces the copper solutions more slowly than grape, invert, and galactose, but more rapidly than milk sugar. ·5 grm. of maltose in 1 per cent. solution equals 64·2 undiluted Fehling; and the same quantity corresponds to 67·5 Fehling, if the Fehling is diluted with four times its volume of water. It is remarkable that dilution of the solutions increases the reducing power; while, with regard to undiluted Fehling, excess of copper appears to have no influence. This fact affords an easy way of estimating maltose by weight; for there is, under these circumstances, and operating with 1 per cent. maltose, only one ratio, viz.—100 of anhydrous maltose equalling 113 copper. It is, of course, necessary to make sure that the copper solution is in excess. The fluids are mixed cold, boiled for four minutes; the suboxide collected on an asbestos filter, reduced in a current of hydrogen, and weighed as metallic copper; or it is also open to the analyst to redissolve the copper from the filter by an acid, and precipitate on a platinum dish by electrolysis.

Soxhlet has also investigated the behaviour of the solutions described with various sugars, and gives the number of cc. of the quicksilver solution reduced by 1 grm. of the different sugars when dissolved so that the solutions are of 1 per cent. strength.

	Knapp.	Sacchse.
Grape sugar,	497·5 cc.	302·5 cc.
Invert sugar,	502·5	376·0
Levulose,	508·5	449·5
Milk-sugar,	322·5	214·5
Galactose,	413·0	226·0
Changed milk-sugar,	448·0	258·0
Maltose,	317·5	197·6

Or, if the reducing power of grape sugar be taken as 100, then the other sugars may be thus compared—

	Fehling undiluted.	Knapp.	Sacchse.
Grape sugar, . .	100·0 cc.	100·0 cc.	100·0 cc.
Invert sugar, . .	96·2	99·0	124·5
Levulose, . . .	92·4	102·2	148·6
Milk-sugar, . .	70·3	64·9	70·9
Galactose, . . .	93·2	83·0	74·8
Changed milk-sugar, .	96·2	90·0	85·5
Maltose, . . .	61·0	63·8	65·0

As to the recognition of the kind of sugar, Sacchse's solution differs in its behaviour with the various kinds more than Knapp's solution, and is, therefore, the best adapted for this purpose.

These solutions possess no advantage over Fehling's in the estimation of sugar, if one kind only is present; but where there are two kinds of sugar in one sample, or, again, where the identity of the sugar is doubtful, then the mercury methods are of very great use and importance. Sacchse recommended the use of his method, combined with that of Fehling, to determine the relative proportions of grape and invert sugar in a mixture. He considered that grape and invert were reduced by Fehling in exactly equal proportions, and by his mercury solution in unequal proportions; but the researches of Soxhlet just detailed show that Fehling does not act in the way assumed by Sacchse, so that the calculation for the amount of sugar in a liquid by the combined method is somewhat different, and must be done according to the following equations.

The general formula is —

$$ax + by = F,$$
$$cx + dy = S,$$

a is the number of cc. Fehling's solution, reduced by 1 grm. of grape sugar.

b is the number of cc. Fehling's solution, reduced by 1 grm. of invert sugar.

c, the number of cc. Sacchse's solution, reduced by 1 grm. of grape sugar.

d, the number of cc. of Sacchse's solution, reduced by 1 grm. of invert sugar.

F, the number of cc. of Fehling's solution, used by 1 volume of sugar solution.

S, the number of cc. of Sacchse's solution, used by 1 volume of sugar solution.

x, the amount of the grape sugar in grammes contained in a volume of the sugar solution.

y, the amount of the invert sugar in grammes contained in a volume of the sugar solution.

Since, with the titration of the mixed sugar solutions, equal amounts of the mercury and copper solutions are taken, which use up unequal amounts of the sugar solution, it is most convenient to calculate the number of cc. of Sacchse and Fehling equivalent to 100 cc. of the sugar solution.

Putting Soxhlet's values in place of the symbols, the equation for grape and invert sugar becomes as follows:—

$$210{\cdot}4x + 202{\cdot}4y = F$$
$$330{\cdot}5x + 266{\cdot}0y = S$$

Or if the mixture is lactose and grape sugar, the equation is—

$$210{\cdot}4x + 196{\cdot}0y = F$$
$$330{\cdot}5x + 442{\cdot}0y = S.$$

Therefore, since the F and S are found experimentally, then there are only two unknown quantities, which are easily calculated by the ordinary rules. It is scarcely necessary to observe that the same calculation applies to Knapp's solution, if the proper values are substituted in the formula.*

Soxhlet's method of using Fehling's solution is as follows:—50 cc. of Fehling's solution are heated to boiling, and the sugar solution run in, in the usual way, until the blue colour disappears. This gives the approximate strength of the solution, and it must be now diluted so that there will be about 1 per cent. of sugar in the solution. A second 50 cc. are now taken and heated with the exact number of cc. of the solution, which (supposing it to be accurately 1 per cent.) would throw down all the copper. This heating is to occupy two minutes for invert sugar, grape sugar, and lactose; four minutes for maltose; and six minutes for milk-sugar. The whole fluid is now poured on to a large

	* 100 cc. of Knapp's solution are reduced by	100 cc. of Sacchse's solution are reduced by
Anhydrous.	Milligrammes.	Milligrammes.
Grape sugar, . . .	201·0	330·5
Invert sugar, . .	199·0	266·0
Levulose, . . .	197·0	222·5
Milk, . . .	310·0	466·0
Lactose, . . .	242·0	442·0
Maltose, . . .	315·0	506·0

filter; if the filtrate is greenish, copper is of course present; but if it is yellow still there may be copper dissolved, and a little must be tested in a test-tube with acetic acid and ferrocyanide of potash solution. A dark red colour shows a large amount, a pale red a small amount; but if there is no colour at all the copper is precipitated, if copper was in the solution. In the next experiment a slightly larger amount of sugar is used, but if free from copper then in the next assay 1 cc. of sugar solution less is taken. These titrations (which are very rapidly executed) are continued until in two experiments the addition or subtraction of 1 cc. gives, on the one hand, a copper-free, and, on the other, a trace of copper-containing liquid. In dark liquids the ferrocyanide and other tests of the kind are unsuitable; but in such a case a few drops of the filtrate are put in a test-tube, boiled with a little sugar solution for a minute, and then put on one side to deposit for two or three minutes. The fluid is now decanted, and a little piece of white filter-paper, which has been previously wound round a glass rod, wiped around the bottom, when any oxide of copper which has been deposited adheres to the paper in this way, and is at once discovered.

It may be well to give an example of this method of sugar titration:—10 grms. of commercial starch sugar were dissolved in 250 cc. of water; of this solution 8 cc. decolourised 50 cc. of Fehling. Now 50 cc. of Fehling correspond to about 24 cc. of a 1 per cent. solution of grape sugar. Hence, to make a 1 per cent. solution, 83·3 cc. must be made into 250 cc. by the addition of water. Six experiments were now made with this solution.

(1.) 23 cc. were boiled with a fresh 50 cc. of Fehling, filtrate *blue-green;* therefore, much copper present.

(2.) 24 cc. boiled in the same way, filtrate *greenish.*

(3.) 25 cc., filtrate *yellow;* no copper reaction.

(4.) 24·5 cc., filtrate, with ferrocyanide, *dark red.*

(5.) 24·7 cc., filtrate *clear red.*

(6.) 24·8 cc., filtrate contained no copper.

The true value, therefore, evidently lies between 24·7 and 24·8 cc.; that is, 24·75 cc. Now, since 50 cc. of Fehling is decolourised by 23·75 cc. of a 1 per cent. solution of grape sugar, 24·75 cc. contain ·2375 grm. grape sugar, and 250 cc. (equalling 83·3 cc. of the original sugar solution) equal 2·399 grms.: therefore, 250 cc. of the original solution (containing 10 grms. of substance) contain 7·20 of grape sugar, and the amount of grape sugar in the whole is 72·0 per cent.

(3.) *Gravimetric Processes.*

Gravimetric processes must be substituted for volumetric in cases in which, from the darkness in colour of the fluid, the end reaction would be difficult to observe. One of the best is that recommended by Dr. Pavy:—The ordinary Fehling's solution is boiled in slight excess with the substance containing glucose or lactose, which should be in solution in about 1 per cent. strength, the precipitate of suboxide of copper immediately collected on a filter, made by packing the throat of a funnel with glass wool, the suboxide of copper dissolved by a little peroxide of hydrogen and a drop of nitric acid; and lastly, the copper deposited as copper on a tared piece of platinum foil by electrolysis and weighed. The amount of copper found, multiplied by ·538, gives its equivalent in glucose. Dr. Pavy recommends for the electrolysis the use of a constant battery, consisting of an outer cell charged with bichromate of potash dissolved to saturation in dilute sulphuric acid, an inner porous cell containing a little mercury at the bottom and filled up with water, and having in its centre an amalgamated zinc rod dipping into the mercury. In the outer cell are two carbon plates. However, any other battery will do, or an ordinary platinum dish may be coated with the copper, as described in the article on the "Estimation of Copper" in the second volume of this work. The method is also applicable to the mercury processes just detailed, and either the excess of mercury cyanide in a solution, or the precipitated mercury, can be collected on gold foil or gold capsules.

It is also evident that the copper suboxide, instead of being weighed as copper or oxide, can be collected, washed, redissolved, and estimated volumetrically. One of the best methods under these particular circumstances is to collect, as before, on glass wool, dissolve, by the aid of a gentle heat, in a solution of pure ferric chloride with the addition of a little sulphuric acid, and then titrate the solution of cuprous chloride by a previously standardised solution of permanganate of potash.

(4.) *Physical Processes for the Determination of Sugar.*

The saccharimeters in use are numerous, but those only of Mitscherlich, Soleil, and Jellett will be described here. The polarising instrument of Mitscherlich is extremely simple. (See fig. 14.) It consists of a stationary Nicol's prism in *a*, a plano-convex lens in *b*, and a rotating Nicol's prism *c*. The first prism

polarises the light, and the use of the second is to indicate the plane of the polarised ray coming from the first. The second prism is therefore set in a graduated circle, *dd*, and is provided with an index, *f*, and there is a handle, *e*, which turns both prism and index. If the index be either at 0° or 180°, and an observer look through the tubes towards the source of light, the flame is seen divided by a vertical line into two equal parts; if now the tube, supplied with the instrument, be filled with the liquid to be examined, and interposed between the lens and the second prism, should it contain sugar or other polarising substance, the black stripe is no longer in the middle of the field, and the handle moving the index and prism must be turned until the black stripe is seen; or, if the stripe is broad and undefined, the prism is turned until the exact point is reached in which blue changes into red—the index at this point marking the amount of the polarisation by the scale and the direction; for if the index has to be turned to the right, the polarisation is +, or right-handed; if to the left −, or left-handed.

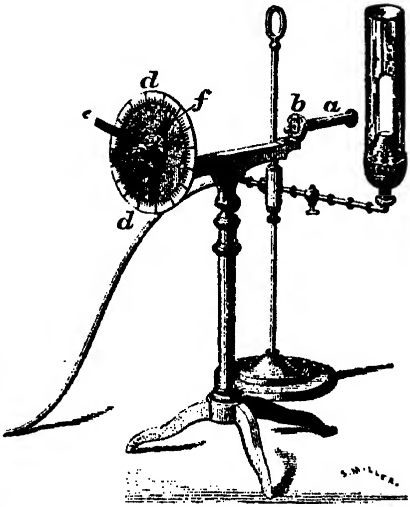

Fig. 14.

In order to make this quantitative, and to estimate the specific *rotation* of a sugar (*i.e.*, the number of degrees of rotation observed when 1 grm. of the sugar is dissolved in 1 cc. of fluid and observed by yellow light through a tube 1 decimetre long), it is necessary to dissolve a known weight of the pure sugar in water; then if the length of the tube be known, and the temperature of the solution and the rotation be observed, all the necessary data are obtained. For example, let the rotation = a, the length of the tube in decimetres = l, the weight of substance in 1 cc. of fluid = p, then the specific rotation for yellow light—

$$\pm \frac{a}{p\,l} \qquad \text{or } (a)_j = \pm \frac{a}{p\,l}$$

the sign $(a)_j$ being in use, signifying yellow light. Or, to take an actual example: 14·3 grms. of a substance dissolved in 100 cc.

(·143 grm. in each cc.), and a 2 decimetre long tube filled with this liquid, the rotation on the scale being 16° to the right, then

$$\frac{16}{0143 \cdot 2} = 55 \cdot 94,$$

and 55·94 is the specific rotation. The best source of light for accurate researches is a Bunsen burner, in the middle of which there is a little pellet of sodium held on a wire. This source of light in formulæ is usually indicated by $(a)_D$.

Provided there be only one sugar in the fluid under investigation, the specific rotation of which is known, the weight of the sugar in 1 cc. of the fluid is estimated by the following formula: $P = \frac{a}{(a)\,1}$, where a equals the observed, and (a) the specific rotation.

Soleil's Saccharimeter.

Soleil's saccharimeter (*see Plate*) consists of three essential parts, two of which are fixed (fig. 1), AB and CD, the other movable, which is inserted between B and C, and which is sometimes the tube BC, 20 centimetres long (fig. 2), and sometimes the tube B′C′ (fig. 3), 22 centimetres long, furnished with a thermometer, T. These tubes are destined to contain the saccharine solutions, the value of which is to be determined.

The movable parts are—

(1.) The small movable tube D′D (fig. 1), carrying the eye-piece, which focuses by drawing in and out.

(2.) The little button V (fig. 4), serves to adjust the zero of the scale with the zero of the indicator.

(3.) The large milled screwhead on the vertical axis H (fig. 1), by which is rendered uniform the tint observed.

(4.) The milled ring B (figs. 1 and 2), by the aid of which they give to this same tint the colour which lends itself best to a precise valuation.

(5.) Lastly, the divided scale RR (fig. 4), on which is read the number giving the richness of the sugar under examination.

The details of operating are as follows:—The lamp is adjusted so that its light traverses the axis. A tube similar to that which contains the saccarhine solution is filled with pure water, and is adjusted in the place provided for it between the ocular and objective portion. Then applying the eye at D (fig. 1), the tube DD′ is either pushed out or in, until the field is seen divided into two equal halves, coloured with one and the same tint, or two different tints separated from each other by a black line, which should be very sharply defined. If, as generally

happens, the two half-discs have not the same tint or shade, the large horizontal button H is turned either way until the desired result is obtained.

It is not only necessary that the two half-discs should have the same tint or colour, but in order to be extremely exact, that tint should be the one most sensible to the eye of the observer; and as all eyes are not equally sensible to the same tint, the proper colour must be found by experiment.

The zero line on the scale must coincide exactly with the black line of the indicator I (fig. 4). If the coincidence is not perfect, it may be established by turning either way the little button V until this is accomplished.

The instrument once adjusted, the examination of the sugar may be commenced.

The tube BC, filled with the saccharine solution, is substituted for that filled with water, or if an inverted sugar is taken, then B′C′ is filled. On now looking through the instrument, it is seen that uniformity of tint no longer exists, and that the two half-discs are coloured by different shades. The uniformity is re-established by turning the large horizontal button H until the two half-discs are again uniform.

As the saccharine solution is mostly coloured, the uniform tint re-established is not in general the sensible tint, to which, however, it is necessary to return, and which the colour of the solution has caused to disappear. The milled head B is then turned to cause the *sensible* tint to reappear; this tint returned, the equality of shade of the two half-discs, if not quite perfect, must be made so by turning again H. It now only remains to read the degree on the scale RR′, to which the index answers; the number corresponding to this degree gives immediately in 100ths the *titre*, or the richness of the solution.

The preparation of the saccharine solutions is as follows:—

(1.) *Normal solutions of pure sugar.*—16·26 grms. of pure sugar are dissolved in water, the volume made up to 100 cc., and observed in a tube 20 cms. in length; marks 100 degrees on the saccharimeter.

(2.) *The raw sugar of commerce.*—16·26 grms. of the sugar are powdered and dissolved in water, and the whole made up to 100 cc.; if the solution is too dark, it may be clarified by sugar of lead. The tube BC is filled with the solution thus prepared and adjusted.

(3.) The next operation is to invert the sugar. 5 cc. of fuming HCl are added to 50 cc. of the sugar solution, and heated in the water-bath up to 68°C.; when that temperature is reached, the solution is put in the tube B′C′, its rotating power (which

is now inverse) observed, and at the same time the temperature at the moment of the observation.*

We have now all the data necessary, and the amount of sugar may be readily found by tables, such as those of M. Clerget, or by the formula as below.

Supposing the number given by the first observation is 75, by the second (inverted) 21, at a temperature of 12°C., the sum of the two numbers (75 + 21) makes 96. Now, in referring to M. Clerget's table, under 12°, or in the third column corresponding to the temperature of 12°, the nearest number to 96 is in this instance 95·6; the horizontal line in which 95·6 is placed is followed, and there is found, first, in the column A, the figures 70 per cent. of pure crystalline sugar; secondly, in the column B, the figures 114·45, placed by the side of 70, which indicates that the saccharine solution examined contains per litre 114·45 grms. of pure sugar. If, however, as sometimes happens, the solution contains a polarising substance not modified by acids, in such a case the difference of the two numbers, and not the sum, is to be taken and dealt with as before. It is scarcely necessary to remark, that if the substance is known to contain only crystallisable sugar, and the tube BC be filled, one observation alone suffices.

If tables are not at hand, the following formula can be used:— Let T be the temperature, S the sum or difference of the two determinations, P the rotatory power, R the quantity of sugar contained in 1 litre of the solution:—

$$P = \frac{2008}{288 - T} \qquad R = \frac{P \times 16{\cdot}350}{10} = P \times 1{\cdot}635 \text{ grms.}$$

Professor Jellett's instrument is a little more elaborate than Soleil's, and of great accuracy. The eyepiece or analyser of the apparatus consists of a suitably mounted prism, made from a rhombic prism of Iceland spar. The rhombic prism is cut by two planes perpendicular to the longitudinal edges, so as to form a right prism. The prism is next divided by a plane parallel to the edge just produced, and making a small angle with the longer diagonal of the base. One of the two parts into which the prism

* Mr. Allen, taking into account the fact that 95 parts of cane sugar equal 100 parts of inverted sugar, gives the following as the specific rotatory power of the principal sugars:—

Cane sugar, ...	+ 73·8°
Invert sugar, ...	− 25·6° at 15°
Dextrose, ...	+ 57·6°
Levulose, ...	− 108·8° at 15°

—*Analyst*, 1880, p. 199.

is thus divided is then reversed, so as to place the base uppermost, and the two parts are connected together.

Another distinctive feature of the instrument is, that the mechanical rotation of the analyser for the finding of any particular plane is dispensed with, this function being transferred to a fluid which has the power of turning the plane of polarisation opposite to that of the solution to be examined. The analysing tube slips into, and moves up and down in, the compensating fluid, so that different thicknesses of the latter fluid can be readily interposed and measured by a scale fixed to the instrument.

The Saccharimètre à Penombrés, of which the principle was enunciated by M. Jellet, as constructed by M. Duboscq, has some very great advantages. It requires the employment of a simple light, and the field does not present to the eye for comparison two different colours, but two intensities, sensibly diverse, of one and the same colour, so that the least variation can be appreciated. The simple light is best obtained by the insertion of a bead of some salt of soda on a platinum wire in the flame of a Bunsen burner.

CONFECTIONERY,—SWEETMEATS.

§ 74. It would take many pages to describe the composition of the various kinds of sweetmeats in commerce: the basis of all is either cane or grape sugar, or honey, flavoured with appropriate essences, and coloured with various colouring matters. A great many common sweetmeats have a most definite composition, and it is evident that a deviation from the ordinary process of manufacture must, if it should take the form of substituting inferior articles for, or the addition of matters giving weight to, that which is ordinarily sold, would be an adulteration. As an example "peppermint lozenges," or "peppermint drops," are composed of albumen, cane sugar, and oil of peppermint. None of these ingredients have any amount of mineral matter, and peppermint lozenges, when burnt, do not leave as much as ·2 per cent. of ash. Since they are sold by weight it is easy to adulterate them by mineral substances; but such an addition would be most decidedly fraudulent, and the analyst may justly certify accordingly.

A large proportion of the common sweets contain nothing else besides sugar, for the manufacturer, by careful heating, is able to impart a quite surprising scale of colours, from the purest white to fawn colour, straw colour, reddish-brown, brown, to almost a jet black, by this agent alone.

SUGAR-CANDY is simply crystals of sugar obtained in a particular way, and is of all colours—from the white candy, largely used for the manufacture of artificial champagne, to all shades of yellow and red. As usually manufactured, the purified sugar solution is concentrated to a specific gravity of 1·420 to 1·450, and then run into copper cones, through which are passed a number of threads; these cones are heated with warm air, and the crystallisation occupies as much as from eight to fourteen days. The composition of white candy, made from pure loaf-sugar, is as follows:—

	Per cent.
Crystallisable sugar,	80·00
Uncrystallisable sugar,	Traces.
Ash,	
Water,	20·00

The coloured candies may contain some mineral matter, and a good deal of uncrystallisable sugar; copper may, as an impurity, be present.

Composition of Sweetmeats Generally.

TOFFY.—Toffy is the melting of sugar with butter, and ether will extract a large amount of fat.

The ice-coating of cakes is composed of white sugar and albumen.

A great many sweets are acidulated with citric acid, and a few have cavities within them, supposed to contain alcohol, but really a little syrup. Gum, tragacanth, citric acid, fruit sugar, gelatine, albumen, fatty and flavouring matters, with the following colouring-matters, make up the usual harmless ingredients of the confectioner's shop:—

Red.—Cochineal, carmine, the juice of beet and of red berries, such as cherries, currants, &c.

Yellow.—Saffron, safflower, turmeric, marigold, Persian berries.

Blue.—Indigo, litmus, saffron blue.

Green.—Spinach juice and mixtures of yellow colours with blue.

Black.—Chinese ink.

Besides these, there are the aniline colours, which, when pure, have not been proved to be injurious.

Analysis of Sweetmeats.

§ 75. The analyst will naturally first turn his attention to the percentage of sugar, and estimate the total amount in the usual way; and, if necessary, investigate by optical and chemical means, whether there is more than one kind of sugar present. The essential oils may be dissolved out by petroleum ether, and identified by their odour; but the colouring-matter will, for the most part, be the chief substance necessary to examine. If the

colouring is only on the external surface, it is better to detach it by scraping or rasping, than to powder the whole substance up, for if the colour is carefully detached as pure as possible, tests may sometimes be directly applied without any further trouble. The colour by treatment with alcohol, with water, and with bleaching powder, is quickly referred either to the organic or to the inorganic division of chemical substances. With regard to organic colours generally, the reader may consult the sections treating of "Colour," where full directions are given for their identification. If, however, the colour is apparently inorganic, then the following substances may be particularly tested for :—

Among RED colours—*iron ;*
,, YELLOWS—*chromate of barium,* and *lead compounds, arsenic* and *antimony ;*
,, GREEN—*arsenic, copper ;*
,, BLUE—*Prussian blue ;*
,, WHITE—*sulphate of barium, salts of zinc.*

A weighed portion of the scraped-off colouring-matter is burned to an ash, which is dissolved in hydrochloric acid, and tested with hydric sulphide, after adding just sufficient soda to so neutralise the acid as to leave only a slight excess. Under these circumstances, lead, copper, or zinc, if present, will be precipitated ; while, if it is strongly acid, zinc would remain almost entirely in solution. Ammonium hydrosulphide is next added to the solution, which has been boiled and filtered from any precipitate ; this reagent will throw down iron, manganese, &c. To test for chromium, it is best to boil the colouring-matter with a solution of carbonate of potassium, when potassic chromate will be formed, which gives, in neutral solutions, a purplish precipitate with nitrate of silver. Barium is easily detected by fusing the ash with carbonate of soda, dissolving the ash in dilute hydrochloric acid, and adding a little hydric sulphate ; a heavy characteristic precipitate of barium sulphate is thrown down. If barium is present, it may exist with evidences of chromium, in which case, in all probability, the colouring-matter was chromate of barium, or if the sweetmeat is not coloured by barium chromate, baryta sulphate may have been added simply to give weight. Arsenic and antimony are best discovered by boiling a little of the colouring-matter with copper-foil [Reinsch's test]; and although this test will not detect quite such a minute quantity as Marsh's test, it is sensitive enough. Copper is also best detected by electrolysis, the substance being placed in a platinum dish, acidified, and then a rod of zinc inserted ; or, the neater plan of connecting the dish itself with a battery may, where appliances are at hand, be preferred.

HONEY.

§ 76. Commercial honey is the saccharine matter collected and stored by one particular species of bee (*Apis mellifica*); but the production of honey is by no means limited to the bee, for there is a honey-ant * in Mexico, which stores a nearly pure syrup of uncrystallised sugar. This is slightly acid in reaction, and reduces salts of silver like formic acid.†

A wasp of tropical America is said to yield a honey in which are found crystals of cane sugar, but the evidence as to this latter point is not decisive.‡ A curious sample of honey has been analysed by A. Villiers. § It was derived from Ethiopia, and is the produce of an insect resembling a large mosquito, which, like our wasp, makes its nest in cavities in the ground. It secretes no wax. The natives call the honey '*tazma*,' and ascribe to it medicinal virtues, especially using it as a cure for sore throat. Its composition is as follows:—

	Per cent.
Water,	25·5
Fermentable sugar (levulose with a sixth of glucose in excess),	32·0
Mannite,	3·0
Dextrine,	27·9
Ash,	2·5
Loss and unestimated,	9·1

The honey contained a non-nitrogenous bitter principle.

The essential constituent of honey is a mixture of dextrose and levulose; it also contains mannite, wax, organic acids, pollen from the flowers, not unfrequently alkaloidal and bitter principles from the plants, possibly derived from the pollen, small quantities of cane sugar, of mineral matter, and invariably minute quantities of alcohol. There exist but few analyses of honey, and those that have been made are incomplete. The best and most reliable are those of Dr. Brown, who estimated the proportion of the different kinds of sugar, &c., as in the following table; but made no determination of the volatile acids, of the alcohol, nor of the amount of mannite. The analyses are, however, quite complete enough to give an idea to the food-analyst as to what proportion of the main and valuable constituents he is likely to find in genuine honey.

* The *Myrmecocystus Mexicanus*. There are two kinds of workers—one the active form, the other sedentary—which produce the honey. The latter is the larger, and has a tumid abdomen; it never quits the nest. The honey is discharged into proper receptacles, and from it the Mexicans make a pleasant drink.

† H. Marsten, *Pogg. Ann.*, c. 550.

‡ G. M. Wetherell, *Chem. Gaz.*, 853, 72.

§ *Compt. Rend.*, lxxxviii. 292, 293.

TABLE VIII.—COMPOSITION OF VARIOUS KINDS OF HONEY.

	English.	Welsh.	Normandy.	German.	Greek.	Lisbon.	Jamaica.	California.	Mexican.
Water expelled at 100°,	19·10	16·40	15·50	19·11	19·80	18·80	19·46	17·90	18·47
Water expelled at a much higher temperature and loss,	7·60	6·56	4·95	11·00	7·80	6·66	7·58	8·13	10·03
Levulose,	36·60	37·20	36·88	33·14	40·00	37·26	33·19	37·85	35·96
Dextrose,	36·50	39·70	42·50	36·58	32·20	34·94	35·21	36·01	38·47
Cane sugar (?)	doubtful	—	—	—	—	1 20	2·20	—	doubtful
Wax, pollen, and insoluble matter,	good trace	trace	slight trace	trace	·05	1·9 nearly	2·10	good trace	trace
Ash,	·15	·14	·17	·17	·15	·14	·26	·11	·07

It will be noticed that the percentage of total glucose varies within very wide limits, the highest number being 79·38, the lowest 68·40 per cent.—a range of nearly 11 per cent. Doubtless the quantity of sugar stored by the bee depends on the age of the insect, "virgin honey" being notoriously of a better flavour and quality than that produced by old bees; it also depends on the nature of the country, and the quality and quantity of food of the bee. The relative quantities of dextrose and levulose range in the table somewhat widely; but if the whole nine analyses are taken, the mean gives nearly equal proportions of dextrose and levulose.

The specific gravity of virgin honey is from 1·425 to 1·429; that of honey from old bees, 1·415 to 1·422. According to Buchner, some forms of honey reach a specific gravity of 1·440; the rotation of a polarised ray, produced by a solution of 16·26 grms. of crude honey, is generally from $-3^{\circ}{\cdot}2$ to -5° at $15^{\circ}{\cdot}5$ [*Brown*].

The properties of dextrose and levulose have been already described. The other saccharine constituent of honey—mannite, $C_6H_{14}O_6$—crystallises in four-sided prisms, is soluble in 80 parts of alcohol of specific gravity 0·898, and in 1·400 parts of absolute alcohol; in boiling alcohol it is more soluble, but in ether it is quite insoluble, and may be precipitated from alcoholic solution by ether. It has no action on polarised light. Its melting point is from 160° to 165°; at 200° it boils, and may be distilled, a portion being decomposed; at higher temperatures it carbonises. It does not reduce cuprous oxide. All these properties readily distinguish it from the other sugars. Chemically speaking, mannite is a hexatomic alcohol. Mannite may be separated from honey by boiling a weighed quantity of the honey with alcohol, evaporating down the alcoholic extract to dryness, and boiling this extract with absolute alcohol, concentrating the alcohol solution, and precipitating with ether. It is also probable that mannite might be separated from the other sugars by distillation in a vacuum, but the author has not proved it by experiment. Finally, it is possible to destroy all fermentable sugars by fermenting them with yeast. This done in the ordinary way is tedious and imperfect; but if plenty of yeast be used, and the fermentation be allowed to go on in a vacuum, the alcohol and carbon dioxide are continually removed, and the process is not only speedy, but complete.*

Honey is a substance likely to be much adulterated. The usual list comprises a number of starch-holding substances, all of them easy of microscopical detection; but the most common

* Sur la fermentation alcoolique rapide. M. J. Boussingault, *Comptes Rendus*, t. xci., 373.

adulteration is, without doubt, syrup made of cheap sugar. There is, indeed, a commercial American artificial honey, which is entirely composed of glucose syrup, while the comb is also artificial, and made of paraffin. The appearance of both comb and syrup is said to be superior to that of natural honey. In examining honey for adulteration, it will be necessary to make a quantitative analysis of the sugar it contains, and a microscopical examination; if neither by the microscope nor by saccharimetry any marked deviation from normal honey is observed, a further analysis will scarcely be necessary. If, on the contrary, by the absence of grains of pollen, by the presence of a large percentage of cane sugar, or by any other deviation from normal honey, a fraud is suspected, it may be necessary to make a very complete analysis. With regard to the artificial American honey, the presence of paraffin in the comb may be easily ascertained. Pure bees'-wax melts at 62° to 65°. Its specific gravity is ·962; it contains cerotic acid, myricine, as well as ceroleine; and, like other fatty matters, it is attacked and blackened by warm sulphuric acid. Paraffin, on the contrary, remains unacted upon, so that this test alone will suffice either to detect paraffin when pure, or to separate it from other matters, such as waxes and fats, which are carbonised by sulphuric acid.

TREACLE, MOLASSES.

§ 77. Treacle, molasses, golden-syrup, and similar terms, are used to denote a sweet syrup which is produced in the manufacture of sugar, and contains a mixture of sugar, partly cane and partly fruit; but the cane sugar, owing to certain salts and impurities, is uncrystallisable. The composition of these brown syrups varies according to the manufacture from which they are derived. The cheapness of treacle, &c., is such that there is no very great temptation to adulteration, and no conviction under the Sale of Food and Drugs Act has hitherto been obtained for adulterated molasses or treacle. The probable mode of adulterating the treacles would be by diluting with water. Cane-sugar molasses is alone used as an article of food, beet-root sugar molasses having an unpleasant taste.

Some analyses, made a few years ago by Dr. Wallace,* of molasses, treacle, and golden-syrup, are as follows:—

* "The Sugar Cane." 1869.

TABLE IX.

	W. Indian Molasses.	Treacle.	Golden Syrup.	Beet Sugar Molasses.
	Per cent.	Per cent.	Per cent.	Per cent.
Cane sugar,	47·0	32·5	39·0	46·7
Fruit sugar,	20·4	37·2	33·0	·6
Extractive and colouring-matter,	2·7	3·5	2·8	15·8
Salts,	2·6	3·4	2·5	13·2
Water,	27·3	23·4	22·7	23·7
	100·00	100·00	100·00	100·00
Specific gravity,	1·360	1·430	1·415	1·405

The ash of beet molasses has the following composition:—

	Per cent.
Potassic chloride,	18·70
Potassic sulphate,	4·18
Potassic carbonate,	53·80
Sodic carbonate,	20·81
Calcic carbonate,	·35
Magnesic carbonate,	·27
Moisture and loss,	1·89

JAM.

§ 78. Jam consists of various species of fruit preserved by boiling in strong syrup. Most jams are very readily adulterated, since any tasteless vegetable tissue, such as vegetable marrow, turnips, &c., when mixed in jam cannot be readily detected by the palate. The chemical composition of the various jams is simply the chemical composition of the fruit juice and fruit itself, with the loss of a few volatile constituents and the addition of cane sugar. The latter may be in part inverted by the action of the organic acids or ferments so constantly found in fruit. The detection of adulterations of jam is mainly microscopic; but, at the same time, in many cases a careful observation of the absorption-spectrum will assist the diagnosis. In order to carry out this successfully, in addition to the precautions before described, it will be safest in all cases to use comparison liquids; and those who devote themselves to this study, should have at hand a variety of genuine jams of different ages. The mean composition of the more common kinds of fruits is detailed in the following table [*König*]:—

TABLE X.—100 PARTS OF THE SEED FRUIT.

	Water.	Nitrogenous substances.	Free acid.	Sugar.	Other non-nitrogenous matters.	Woody fibre, &c.	Ash.
Apple, ...	83·58	0·39	0·84	7·73	5·17	1·98	0·31
Pear, ...	83·03	0·36	0·20	8·26	3·54	4·30	0·31
Plum, ...	81·18	0·78	0·85	6·15	4·92	5·41	0·71
Prune, ...	84·86	0·40	1·50	3·56	4·68	4·34	0·66
Peaches, ...	80·03	0·65	0·92	4·48	7·17	6·06	0·69
Apricots, ...	81·22	0·49	1·16	4·69	6·35	5·27	0·82
Cherries, ...	80·26	0·62	0·91	10·24	1·17	6·07	0·73
Grapes, ...	78·17	0·59	0·79	24·36	1·96	3·60	0·53
Strawberry, . . .	87·66	1·07	0·93	6·28	0·48	2·32	0·81
Raspberry, . . .	86·21	0·53	1·38	3·95	1·54	5·90	0·49
Bilberry, ...	78·36	0·78	1·66	5·02	0·87	12·29	1·02
Blackberry, . . .	86·41	0·51	1·19	4·44	1·76	5·21	0·48
Mulberry, ...	84·71	0·36	1·86	9·19	2·31	0·91	0·66
Gooseberry, . . .	85·74	0·47	1·42	7·03	1·40	3·52	0·42
Currant, ...	84·77	0·51	2·15	6·38	0·90	4·57	0·72

Brief Notes of the Microscopical Structure of Certain Fruits.

§ 79. *Apples and Pears.*—Both apples and pears contain numerous dotted ducts and spiral vessels. There is no very distinctive peculiarity about these ducts, but in the core will be found a strong horny membrane with spiculated cells, crossing one another at right angles, forming altogether a very singular tissue, and one which, once seen, can always be recognised.

Damson.—The skin of the damson is composed of at least two distinct species of cells underlying the transparent epidermis. One kind is a double row of reddish-purple oblong or oval cells, having, when seen in section, an average length of ·00232 inch, and an average breadth of about ·000928 inch; seen from above (as in tearing off a shred of the tissue) they form a beautiful five- and six-sided mosaic pattern, the size of the cells being from about ·000928 to ·00116 inch. The blue cells are very similar in shape and size to the reddish-purple; below the blue there are some loose cells containing chlorophyll. Hence the beautiful colour of the damson is the combined effect of the blue, the red, and the green shining through the transparent epidermis. The pulp contains the usual large colourless globes or cells, of ·0116 inch average diameter (*b*, fig. 15). Spiral vessels are numerous;

stomata are occasionally to be seen on the surface of the dark-coloured epidermis. The breadth or thickness of the skin is ·00814 inch. By the use of bleaching powder, a small portion of the skin may be deprived of its colour, either partially or wholly, according to the judgment of the operator, and then will be seen a mapping out of the whole surface into lobes by cells so placed that they form a network.

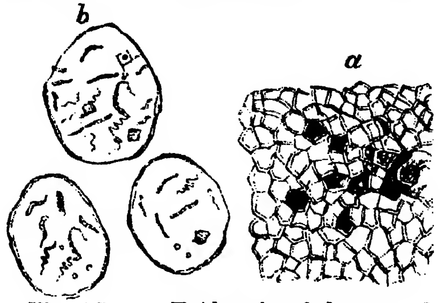

Fig. 15. -*a*, Epidermis of damson; *b*, pulp cells, ×115.

Plum.—There are at least three distinct structures to be seen in the boiled and preserved plum :—1. The epidermis, consisting for the most part of a pavement-like layer of little square or irregularly oblong cells, filled with a granular matter (*c*, fig. 16), the size of the cells averaging from about ·000696 to ·00116 inch; the general distribution of these cells is somewhat circular. Scattered tolerably uniformly are patches of a deeper colour with larger cells, the patches being irregularly circular, and the centre of the patch an empty space, which possibly is a much deformed stoma. The pulp consists of the very common large globular cells (*a*, fig. 16), of about ·12 to ·14 inch diameter, almost perfectly transparent, with a shrivelled mass within. Lastly, there are some beautiful masses of compound cells, varying in size from ·016 to ·48 inch (*b*, *b*, fig. 16), the length usually being from one and a half to three times the breadth. These compounds are either prismatic in shape or oval, while a few resemble long tubes. The number of cells thus bound together is very variable, since from seven up to twenty-seven may be counted on one side. The little cellular members of the composite are five-sided cells of an average length of ·06 inch.

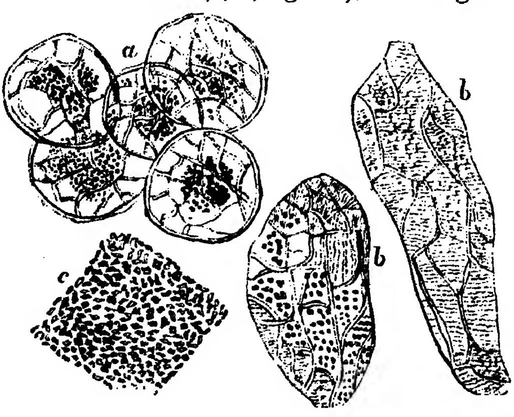

Fig. 16.—Structures found in the plum, ×115. *a*, Pulp cells; *b*, *b*, compound cells; *c*, a portion of epidermis.

Oranges—Lemons; Marmalade.—Marmalade is made by preserving sliced up oranges or lemons, or both combined, in a strong syrup. Orange marmalade is properly made from Seville oranges only, lemon marmalade from lemons only. It is not practicable to distinguish by the microscopic structure alone whether the substance is orange or lemon, or to what species the orange or the lemon belongs. It is, however, most easy in marmalades to recognise substances foreign to marmalade, because the structure of the vegetable tissues used is very distinctive. Good marmalade is wholly composed of fine sections of the fruit: on selecting the thinnest of these sections, or (what amounts to the same thing) cutting and preparing a section, there will be three structures to notice. It will be observed that the colour layer is very thin, and composed of layers of yellow cells (*a*, fig. 17), many filled with oil, and here and there large cavities, covered with a thin transparent epidermal layer. The size of the cells is small, about ·000147 inch in diameter. Beneath the yellow layer there is a deep layer of colourless cells, traversed by a network of bundles of vessels, each bundle consisting of a dozen or more spiral vessels, of small diameter, in the midst of the ordinary elongated fibre-like cells. In this layer are large cavities, ·0415 inch diameter or more, and around these cavities the cells are applied in concentric layers. The pulp of the orange presents a number of soft and thin-walled cells without any very distinctive peculiarity. Large spirals, large oval cells and structures, dissimilar to the above, will be suspicious signs, and will denote adulteration.

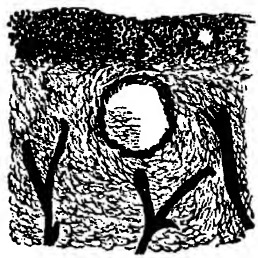

Fig. 17.—Section of rind of orange, × 20. *a*, Layer of yellow cells; *b*, inner white cortex, showing a cavity and vascular twigs.

The Strawberry may be readily distinguished under the microscope by the great number of very small seeds which are scattered on the exterior of the fruit. These seeds are pyriform and very regular in size, being about ·038 inch wide at the broadest end, and ·07 inch in length. The coat of the seed is almost smooth; under a high magnifying power it may, however, be seen to be slightly tuberculated. Each seed is attached to the central part of the fruit by means of a vascular bundle formed of delicate fibres and spiral vessels; and the consequence of this structure is, that the strawberry is full of spiral vessels, all of minute size and very transparent. The cells seen when jam is examined are, for the most part, collapsed and shrivelled; those that are not so

are large oval or pyriform cells, often containing shrivelled cell contents. Common measurements of these cells are ·008 inch small diameter, ·0176 inch long diameter for the oval cells, and for the pyriform ·0136 inch broad end, ·0184 long diameter.

Fig. 18.—*a*, Pulp cells of strawberry, × 115; *b*, strawberry seed, × 20.

The Raspberry has its seeds reticulated, and in most jams the form of the fruit is preserved quite sufficiently for recognition.

The Gooseberry has an epidermis in which can be seen a mosaic pavement of cells, and the fruit also possesses clavate hairs.

The Blackberry—the seeds are reticulated, and the cuticle covered with stellate hairs.

Currants.—Both the black and the red currant are similar in structure: the epidermis is covered with an excessively thin membrane, showing sinuous wavy divisions, and set with simple hairs. Beneath the outer membrane are the colour layers, consisting of little square masses with rounded angles about ·00029 to ·00039 inch diameter (*a*, fig. 19). The pulp is made up of thin-walled cells, and, lastly, here and there may be found peculiar compound bodies, *b*, attached to the inner layer of the epidermis. These are about ·0058 inch in length and ·0015 inch in breadth, and are formed of a number of oblong cells. So far as known, these bodies are found only in the currant.

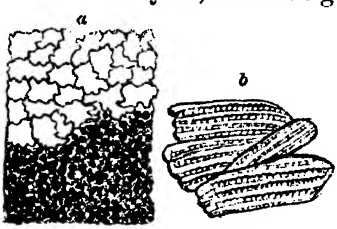

Fig. 19.—*a*, A shred of epidermis, showing the sinuous markings in one portion, and the under layer of cells in another; *b*, the compound bodies, × 115.

STARCH, $C_6H_{10}O_5$.

§ 80. It is convenient to consider the starches together, more especially as, however varied in form, the chemical composition of all starch is very similar, if not identical.

Every starch corpuscle is composed of at least two probably isomeric bodies, the one "*granulose,*" soluble in saliva, and

coloured blue by iodine; the other coloured by iodine pale yellow, and only becoming blue after the addition of sulphuric acid; it is fully soluble in ammoniacal oxide of copper, and appears to agree very closely with the characters of *cellulose.*

These two substances may be most readily separated by diluted chromic acid, which dissolves granulose very easily, whilst cellulose remains unaltered. All starch is very hygroscopic: wheat starch, dried in a vacuum, still contains 11 per cent. of water, and air-dried from 16 to 28 per cent. of water. Starch is insoluble in cold water or spirit. Some chemists, indeed, assert that if finely powdered in agate mortars, or with quartz sand, a small portion dissolves; others contend that this is no true solution, but the starchy matter in a state of most minute division. If warmed with water, the starch granules swell, and when heated up to 100° most starches form a semi-solution in water. True compounds of starch with bases are scarcely established. Lime and baryta appear to form weak unions, and the intense colour produced by iodine, as well as bromine, seems to point to the formation of haloid combinations. Fritsche, indeed, states that he has isolated the iodide and the bromide of starch, the former containing ten equivalents of starch and one of iodine.

Starch heated in closed tubes up to 100°C. changes gradually into soluble starch. If the temperature is raised up to 160° or 200°C., it forms a transparent mass, consisting wholly of dextrine. At 220° to 280° still further change is produced, and the result is *pyrodextrine*, a substance easily soluble in water (but insoluble in absolute alcohol and ether), and with the composition of $C_{48}H_{36}O_{36}HO$. At still higher temperatures there is carbonisation, and the formation of products similar to those caused by the decomposition of sugar.

Starch is easily changed into sugar by the action of dilute mineral acids, as well as by oxalic acid, aqueous chloride of zinc, and by certain ferments—diastase, saliva, yeast, &c.

The estimation of starch in organic bodies generally is best carried out as follows:—The powdered and dried substance is heated in a 5 per cent. solution of caustic potash in absolute alcohol, in a closed tube, in the water-bath for twenty-four hours, and filtered while hot. The residue is washed first with absolute alcohol, and then with ordinary alcohol, dried, and heated with a solution of 2 per cent. hydrochloric acid, in a flask fitted to a vertical condenser, until a blue colour is no longer produced by iodine. (See also p. 113.) The sugar is then estimated in the ordinary way.

Microscopical Identification of Starches.

The successful microscopical examination of starches requires practical study, and those who desire to identify them must use all drawings and descriptions as guides merely. It is not easy to preserve starches mounted as microscopical objects,* and the analyst is therefore recommended to fit up a little case, in small, wide specimen-tubes, so that he can have at hand a sample of every kind of starch possible to be obtained. These samples should be arranged in the five following classes, partly based on Dr. Muter's † classification.

A high magnifying power is not required, save for the very minute starches, such as rice and pepper. For ordinary work a magnifying power of 250 diameters is ample. Dr. Muter's classification of starches was founded on observations with a B micrometer eyepiece and a $\frac{4}{10}$-inch power.

It is also useful to observe the various samples of starch, and make tables of their dimensions. The proper way to do this is to put the smallest possible quantity of the well-mixed starch on a glass slide, add a droplet of distilled water, cover with a thin glass, take the exact size of all the starches in the field, enumerate them, and work them out into percentages for future reference.

The illumination of starches is to be particularly attended to. The light must strike obliquely through the granules, in order to observe the rings, which are by no means so easily seen as diagrams would indicate.

Polarised light is also useful, especially in the diagnosis of certain starches. Thus, the polarised starch of wheat, when examined in water, exhibits a dull cross; that of jalap, in shape and size like wheat, polarises brightly. Polarised light, in conjunction with a selenite plate, will also be found of great service. Red and green selenites are best, and give a beautiful play of colours with the arrow-roots and potato starch; while the starches of wheat, barley, rice, and oats, scarcely show any colour. The whole of the starches of the Leguminosæ are, so far as they have been hitherto examined, likewise destitute of this power of brilliant colouration. A $\frac{1}{4}$-inch object-glass, with an A eyepiece, will be found better adapted for this method of research than higher powers.

If adulteration in any case has been made out, approximative quantitative results may be obtained by making a standard

* According to Muter, a mounting medium of 1 part of glycerine to 2 of water preserves the characters of starch longest.

† "Organic Materia Medica." London, 1878.

mixture of the genuine starch with the adulterant found, and then counting the individual grains in the microscopic field. Thus, for example, supposing oatmeal to be found adulterated with barley-starch, and from a preliminary examination the mixture is thought to be 40 per cent., we proceed as follows :—

Pure barley-meal and oatmeal are carefully dried at 100°C. and mixed so that the mixture is exactly 40 per cent. A few grains of this powder are now rubbed up with glycerine and alcohol into a smooth paste, which is then further diluted to a certain bulk, a drop taken out with a glass rod, and covered with a glass, which is gently pressed down. The number of grains of barley and oat starch are now counted, and their relative proportion noted, and an exactly similar process is applied to the oatmeal in question.* If proper care be taken to repeat the experiments, the result is a near approximation to the truth. If photographs are taken of these mixtures, they are always at hand for reference, and much time is saved.

DIVISION I.—Starches showing a Play of Colours with Polarised Light and a Selenite Plate.

Class I.—*The hilum and concentric rings clearly visible, all the starches oval or ovate. The group includes tous les mois, potato, arrow-root, calumba, orris-root, ginger, galangal, and turmeric.*

Tous les mois, or **Canna arrow-root**, is furnished by the *Canna edulis*, nat. order *Marantaceæ*. The granules vary in diameter from ·0469 to ·132 mm. [·0018 to ·0052 inch]. They present themselves under several forms, the smaller being granular or ovoid, the larger pyriform, whilst the largest granules are flat, oval, and pointed at their extremities. The hilum is annular, eccentric; the rings are incomplete, extremely fine, narrow, and regular. The starch dissolves easily in boiling water; solution of potash causes the granules to swell rapidly, and gives to the hilum and lines remarkable clearness.

Tous les mois can only be confused with the potato; the size is the chief distinction. The granules burst in water at 72°., and they give a more regular cross when examined by polarised light than those of the potato.

Curcuma arrow-root, which is also called East Indian (though the arrow-root ordinarily sold as East Indian is a Maranta), is furnished by the *Curcuma angustifolia*. The granules are elon-

* See a paper by E. L. Cleaver, F.C.S., *Analyst*, January 31, 1877.

gated triangular, or irregularly oval, flattened, and almost transparent. The normal measurement varies from ·0304 to ·0609 mm. [·0012 to ·00238 inch]. The hilum is eccentric, not very distinct; the concentric rings are clearly visible, and form segments of a circle. The application of heat or a solution of potash deforms the grains in a very irregular manner; they begin to swell about 72°.

Maranta arrow-root, syn. *Jamaica, St. Vincent*, is derived from *Maranta arundinaceæ*. The granules are somewhat ovoid flattened, and tending to a triangular shape in the larger, but the smaller may be circular. The concentric layers are always visible and numerous, but not very marked. Nucleus is central, or about $\frac{1}{6}$ eccentric—in some circular, in others linear; from the nucleus a little slit, filled with air, often goes to the edge. Length of granule 0·010 to 0·070 mm., average 0·036 mm. [= ·00138 inch]. Tumefaction in water begins at 70°. The specific gravity of the starch taken in petroleum or benzole is 1·504; if dried at 100°, 1·565.

Natal arrow-root is probably the produce of *Maranta arundinaceæ*, the same plant from which Maranta itself is derived, but growing in a different climate. The majority of the granules are broadly ovate, but some are occasionally circular. The dimensions are from ·0327 to ·0375 mm. [·00129 to ·00148 inch]. The eccentricity of the hilum ranges between $\frac{1}{15}$ and $\frac{1}{3}$. The laminæ appear under water with special clearness, and on this account granules of Natal arrow-root have been frequently mistaken for those of the potato.

Potato starch, syn. *Potato arrow-root*.—The starch derived from the potato (*Solanum tuberosum*). The granules vary greatly in shape and size, some being small and circular, others large, ovate, and oyster-shaped. The hilum is annular, and the concentric rings incomplete. In the larger granules the rings are numerous and distinct. The normal dimensions are ·06 to ·10 mm. [·0024 to ·0039 inch]. The eccentricity averages $\frac{1}{6}$. The granules float on chloroform.

Potato starch is frequently used as an adulterant of the arrow-roots. The most reliable method of examination is careful microscopic observation, but there is also a different behaviour with regard to reagents, viz.:—

(1.) Maranta arrow-root, mixed with twice its weight of hydrochloric acid, produces a white opaque paste, whereas potato starch treated similarly produces a paste transparent and jelly-like.

(2.) Potato starch evolves a disagreeable and peculiar odour when boiled with dilute sulphuric acid, which is not the case with arrow-root.

(3.) An acrid oil may be extracted from the starch of the potato, but not from that of the Maranta.

Ginger.—The granules are variable in shape, but characteristic. The usual form may be described as shortly conical with rounded angles; the hilum and rings are very faint. Measurement about ·0376 mm. [= ·00148 inch].

The remaining starches belonging to this group are distinguished as follows:—

Galangal granules, skittle-shaped, with faint incomplete rings, an elongated hilum, with a normal measurement of ·0342 mm. [·00135 inch].

Calumba.—The starch granules of Calumba are variable in form, most of them are pear-shaped. They have a semilunar hilum, and faint complete rings. The measurement is about ·0469 mm. [·00185 inch].

Orris-root.—The starch granules are of a characteristic, elongated, oblong shape, with a faint hilum. Measurement ·028 mm. [·00092 inch].

Turmeric has oval, oblong, conical granules, with the rings well marked and incomplete. Normal measurement ·0376 mm. [·00148 inch].

DIVISION II.—Starches showing no Iridescence, or scarcely any, when Examined by Polarised Light and Selenites.

Class II.—*The concentric rings all but invisible; hilum stellate. To this group belong the starches of the bean, pea, maize, lentil, dari, and nutmeg.*

The nucleus of the Leguminosæ is seen usually as a long, more or less stellate, air-filled black hollow. The concentric layers are recognisable if the starch is treated with chromic acid.

The starch from the *bean, pea,* and *lentil* are in shape oval, oblong, and almost identical; but the bean and pea have both a stellate hilum, whilst that of the lentil is a long depression. The granules of the bean are fairly uniform in size, averaging ·0343 mm. [·00135 inch]; those of the pea, on the other hand, are very variable in size, ranging from ·0282 to ·0177 mm. [·00111 to ·0007 inch], the smaller size predominating. The lentil granules average ·0282 mm. [·00111 inch]. The granules of the *nutmeg* are of small size and of characteristic shape. Measurement about ·014 mm. [·00055 inch]. The starch from the *dari* is in small elongated hexagons; average size ·0188 mm.

[·00074 inch]. The starch from *maize* varies in shape from round to polyhedral; the granules are the same size as those of the dari; the distinguishing mark is the rounded angles of the polygonal granules.

CLASS III.—*Starches having both the concentric rings and hilum invisible in the majority of granules. This important class includes wheat, barley, rye, chestnut, acorn, and a variety of starches derived from medicinal plants, such as jalap, rhubarb, senega, &c., &c.*

Wheat starch is extremely variable in size, being from ·0022 to ·052 mm. [·00009 to ·0019 inch]. The granules are circular, or nearly so, and flattened. Polarised light shows a cross, but in water the effect is not great.

Barley.—The granules of barley are of fairly uniform size—viz., ·0185 mm. [·00073 inch], but a few measure ·07 mm. The shape of the starch is that of slightly angular circles.

Rye.—Rye starch is similar in shape to barley starch. The measurements are from ·0022 to ·0375 mm. [·00009 to ·00148 inch]. The small granules are perfectly round, and here and there cracked.

Chestnut.—The starch grains vary much in form; they are round or elliptical, or three- or four-angled, with the angles rounded. In the place of a nucleus there is almost always a central hollow filled with air. The size is small and regular, being from ·0022 to ·022 mm. [·00009 to ·0009 inch], and this regularity of size is the chief means of distinction.

Acorn.—The starch granules of the acorn are almost round, or round-oval. A nucleus may be made out after treatment with chromic acid; eccentricity ¼. Normal measurement ·0188 mm. [·00074 inch].

CLASS IV.—*All the granules truncated at one end. This class includes sago, tapioca, and arum, besides several drugs—viz., the starches from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.*

Sago.—A starch obtained from the pith of certain species of palms, especially *Sagus levis*, and *S. Rumphii.* It exists in commerce as *raw* and as *prepared* sago; both have oval-ovate granules, the normal measurements of which are from ·0282 to ·0660 mm. [·00111 to ·0026 inch]. There is a circular hilum at the convex end of the raw sago granules, and rings are faintly visible; but

starch granules from prepared sago have a large oval or circular depression, covering nearly one-third of each granule.

Tapioca is a starch furnished by the *Manihot utilissima*, which is more or less altered by heat, having been dried on hot plates. This causes some of the granules to swell, and thus renders indistinct in some cases the original structure. The starch is in groups of two to eight, or in isolated granules. When resting on its flat surface, the granule shows a little circle, and round this is a broad flat zone; but if resting on its curved surface, the granule shows contours varying from a kettle-drum to a sugar-loaf shape; and it can then be recognised that the nucleus does not lie in the centre, but in the axis of the granule, and always nearer to the curved than to the flat surface. A conical hollow exists under the nucleus, filled with a substance slightly refracting light. The normal measurement is from ·0140 to ·01879 mm. [·00055 to ·00074 inch].

Arum starch, sometimes called *arum arrowroot*, has somewhat smaller grains than tapioca; they are truncated by two facets; the hilum is eccentric. The normal measurement is about ·014 mm. [·00056 inch].

CLASS V.—*In this class all the granules are angular in form; it includes oats, tacca, rice, and pepper, as well as ipecacuanha starch.*

Oat starch or meal.—The starch of the oat is mostly polyhedral, being irregularly from three- to six-sided—·0044 to ·03 mm. [·00017 to ·00118 inch]. The principal starch with which it has been found adulterated is barley; but great caution must be used, for oatmeal contains little round masses extremely similar to barley.

Tacca arrow-root, also called *Tahiti arrow-root*, is extracted from the *Tacca Oceanica* and *pinnatifida*. The granules, when viewed sideways, are muller-shaped, with truncate or dihedral bases; when seen endways they appear circular, occasionally angular or polyhedral; sometimes a sort of contraction gives them a sub-pyriform appearance. The hilum is well developed, often starred. The normal measurement is from ·0094 to ·0190 mm. [·00037 to ·00075 inch]. It may be confused with maize starch, but tacca has *sharp* angles; maize, *rounded*.

Rice starch.—Each individual grain is polygonal, mostly five- or six-sided, here and there three-sided. If a high magnifying power, such as $\frac{1}{8}$ or $\frac{1}{12}$, be used, a starred hilum may be seen. The normal measurement is from ·0050 to ·0076 mm. [·0002 to ·0003 inch].

Pepper.—The starch of pepper is in small polygonal granules, each of which, with a high magnifying power, is seen to possess a hilum. The normal measurement is from ·0050 to ·0005 mm. [·0002 to ·00002 inch].

§ 81. Vogel has given the following table to assist in the diagnosis of different starches :—

A. GRANULES, SINGLE THROUGHOUT, BOUNDED BY ROUNDED SURFACES.

I. Nucleus central, layers concentric.

(*a.*) For the most part round, at the side lens-shaped.

Nucleus round or a radiating slit.

(1.) Large granules, 0·0396 to 0·0528 mm. [·0015 to ·002 inch]—**RYE STARCH.**

(2.) Large granules, ·0352 to ·0396 mm. [·0013 to ·0015 inch]—**WHEAT STARCH.**

(3.) Large granules, ·0264 mm. [·001 inch]—**BARLEY STARCH.**

(*b.*) Egg-shaped, kidney-shaped, mostly a long, often a ragged slit ; diameter of starch, ·032 to ·079 mm. [·0012 to ·003 inch]—**LEGUMINOUS STARCHES.**

II. Nucleus eccentric, rings markedly eccentric or meniscus-shaped.

(*a.*) Granule not flattened, or only slightly.

(1.) Nucleus mostly at the smaller end, ·06 to ·10 mm. [·0023 to ·0039 inch]—**POTATO STARCH.**

(2.) Nucleus mostly at the broad end or towards the middle, ·022 to ·060 mm. [·0008 to ·0023 inch]—**MARANTA STARCH,** (W. India arrow-root).

(*b.*) Granule more or less markedly flattened.

(1.) Many of the granules drawn out more or less at one end into a short point near the nucleus ; at the most, ·060 long [·0023 inch]—**CURCUMA** ; at the most ·132 mm. [·0041 inch]—**CANNA.**

(2.) Many lengthened into a disc, bean, or club-shaped form ; nucleus near the broader end, ·044 to ·075 mm. long [·0017 to ·0029]—**BANANA STARCH.**

(3.) Many markedly kidney-shaped ; nucleus near the edge—**SOUTH AMERICAN ARROW-ROOT** (*Sysirinchium galaxoides*).

(4.) Egg-shaped, one end thinning into a wedge form, placed one against the other, nucleus at the smaller end, ·05 to ·07 mm. [·0019 to ·0027 inch]—**YAM STARCH.**

B. STARCH GRANULES, SINGLE OR COMPOUND. SINGLE STARCHES WITH RELATION TO THE LITTLE GRANULES THEY ARE MADE UP OF. Bounded by even, many-angled surfaces, or partly by rounded surfaces.

I. Granules throughout many-angled.

(1.) With an evident nucleus, largest ·0066 mm. [·00025 inch]—RICE.

(2.) Without a nucleus, the largest ·0088 mm. [·00034 inch]—MILLET STARCH.

II. Among many angular forms also some rounded.

(A.) No drum-shaped starches present, angular forms predominating.

(1.) Without a nucleus, very small, ·0044 mm. [·00016 inch]—OAT STARCH.

(2.) With a nucleus, ·0132 to ·0220 mm. [·0005 to ·0008 inch].

(a.) Evident round nucleus, here and there the smaller combined, granules in variously shaped groups—BUCKWHEAT.

(b.) Mostly a radiating or star-shaped fissure, none of the granules united—MAIZE.

(B.) More or less numerous drum-shaped to sugar-hat shaped granules.

(1.) Numerous eccentric layers. Largest granules, ·0220 to ·0352 mm. [·0008 to ·0014 inch]—BATATA STARCH.

(2.) Without concentric circles, ·008 to ·022 mm. [·0003 to ·0008 inch].

(a.) The slit of the drum-shaped particles enlarged towards the flattened side, ·008 to ·022 mm. [·0003 to ·0008 inch]—CASSAVA STARCH.

(b.) Slit wanting or not large.

(aa.) Nucleus small, eccentric, ·008 to ·016 mm. [·0003 to ·0006 inch]—PACHYRHIZUS ANGULATUS.

(bb.) Nucleus small, central, or wanting.

(aaa.) Irregular many-angled forms, ·009, ·008 to ·0176 mm. [·0003 to ·0007 inch]—SECHIUM STARCH (Cucurbitaceæ).

(bbb.) Only a few angular forms, some with a radiated fissure, ·008 to ·0176 mm. [·0003 to ·0007 inch]—CHESTNUT STARCH.

C. Granules Single and Compound, the Majority Egg-shaped and rounded with Eccentric Nucleus and Numerous Concentric Layers, the Compound Masses composed of a Large Granule and one or a few very Small Flattened Drum-shaped Bodies ·025 to ·066 mm. [·00097 to ·0025 inch]—SAGO STARCH.

Karmarsch has determined the maximum size of some of the starches. Karmarsch's values, as well as Wiesner's, are arranged in the following Table (XI.) They differ in a few instances from the dimensions the author has given at pp. 139–144.

TABLE XI.

	Karmarsch.		Wiesner.	
	mm.	Inch.	mm.	Inch.
General size of potato,	·100	·0039	·06 to ·10	·0024 to ·0039
Maximum, . .	·185	·0079	...	...
Maranta starch, . .	·140	·0055	·01 to ·07	·0004 to ·0028
Hogbean, *Vicia faba*, .	·075	·0029	·065	·0025
Sago, ...	·070	·0027	·033	·0012
Linseed, . . .	·067	·0026	·033 to ·039	·0012
Common bean, . .	·063	·0024	·057	·0021
Pea, ...	·050	·0019	·0283	·0011
Wheat starch, . .	·050	·0019	...	...
Batata, . . .	·045	·0018	·0369	·0014
Rye, ...	...	...	·031	·0012
Oat, ...	...	...	...	...
Maize, ...	·030	·0012	·020	·0007
Tapioca, . . .	·028	·0010	...	...
Rice, ...	...	...	·022	·0008
Barley, ...	·025	·0009	·0203	·0007
Millet, ...	·010	·0004	·009	·0003
Buckwheat, . . .	...	...	...	...

BIBLIOGRAPHY.

AALERS.—Méthode pour essayer la pureté de l'arrowroot. *Archiv. der Pharm.*, *Journ. Pharm. et Chim.*, 4e serie, 1866, t. iii., p. 217.
BÉCHAMP.—*Compt. Rend.*, xxxix. 653; xlii. 1210.
DELFFS.—*Poggend. Annal.*, cix. 648; *N. Jahrb. Pharm.*, xiii. 1.
GREENISH, T.—*Pharm. Journ.* [3], vol. vii., &c.
GUÉRIN, VARRY.—*Ann. Chim. Phys.* (2), lvi. 525; lvii. 108; lx. 32; lxi. 66.
GUIBOURT.—*Ann. Chim. Phys.*, xl. 183.
HANBURY and FLUCKIGER.—"Pharmacologia." Lond. 1874.
HASSALL.—"Food and its Adulterations."
JONES, H. W.—*Pharm. Journ.*, 1876, p. 23.
JESSEN.—*Poggend. Annal.*, cvi. 497; *Journ. Pract. Chem.*, cv. 65.
MASCHKE, J.—*Pract. Chem.*, lvi. 409; lxi. 1.
MUTER, J.—"Organic Materia Medica." Lond. 1878.
NÄGELI.—Die Starke-Mehlkörner. 1858.
PAYEN.—*Ann. Chim. et Phys.* (2), liii. 73; lvi. 337; lxi. 355; lxv. 225; (4), iv. 286. *Compt. Rend.*, xiv. 533; xviii. 240; xxiii. 337; xxv. 147; xlviii. 67.
ROYLES.—"Materia Medica."
SCHARLING.—*Journ. Pharm. et Chim.* [3], 1856. t. ii., p. 246.
TRIPE, I. W.—On the Discrimination of Starches by Polarised Light. *Analyst*, 1879, vol. iv., p. 221.
WIESNER.—Einleitung in die Technische Mikroscopie. 8vo, Wien, 1867.

WHEAT—WHEATEN FLOUR.

§ 82. The wheat cultivated in this country is the *Triticum vulgare*, of which there are two varieties—the *T. æstivum*, or summer wheat, and the *T. hybernum*, or winter wheat. The mean composition of wheat from 250 analyses is as follows [*König*]:—

	Per cent.
Water,	13·56
Nitrogenous substances,	12·42
Fat,	1·70
Sugar,	1·44
Gum and dextrine,	2·38
Starch,	64·07
Fibre,	2·66
Ash,	1·79

These analyses do not include Russian wheat. In the central parts of South Russia a wheat is grown which has an amount of nitrogenous substances quite uncommon—the mean of twenty-four analyses giving a percentage of 3·45 nitrogen and 21·56 nitrogenous substances. The mean composition of the ash of entire wheat is as follows:—

	Winter wheat.	Summer wheat.
Potash,	31·16	29·99
Soda,	2·25	1·93
Lime,	3·34	2·93
Magnesia,	11·97	12·09
Ferric oxide,	1·31	·51
Phosphoric acid,	46·98	48·63
Sulphuric acid,	·37	1·52
Silica,	2·11	1·64
Chlorine,	·22	·48

According to the researches of M. Duvivier, of Chartres, the external part of the envelope of the grain is covered with fatty, odorous, and nitrogenous matters, which are in a particular combination, and form on the grain a very tenacious coating—a sort of preservative, and communicating an odour quite *sui generis*. These substances, which are named *cerealin*, *tritisecaline*, &c., are isolated by treating the entire grain with cold ether, and then allowing the ethereal extract to evaporate spontaneously. However, neither the nature nor even the presence of these matters can be considered satisfactorily established, and further investigation seems necessary.

§ 83. *Constituents of Flour.*—*Flour*, in the common acceptation of the term, is ground wheat freed from bran.

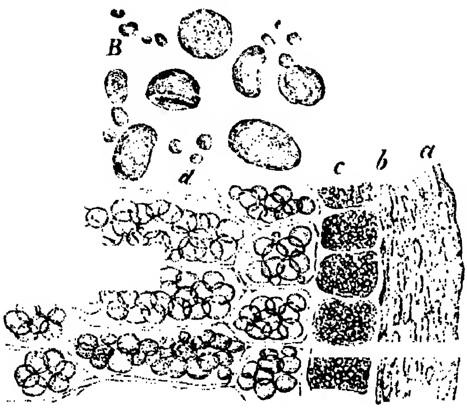

Fig. 20 is a representation of the microscopical structure of wheat when a fine section of the seed is made, × 199. *a* is the cells of the bran; *b* the cells of the thin cuticle; *c* the gluten cells; *d* the starch cells; B, wheat starch, × 350.

The *physical characters* which flour should possess are as follows:—It should be an almost perfectly white, fine powder, with only the slightest tinge of yellow the odour should be sweet, and it should be free from acidity. It should exhibit no trace of bran when pressed smooth with a polished surface; and it should have a certain amount of cohesiveness sufficient to retain for some time any shape impressed upon it by squeezing. The microscopical characters of good flour are: the absence of foreign starches, of fungi, &c., and the presence alone of the elements of ground wheat. (See pp. 142, 144, and 146, for measurements of the starches.)

The chemical composition of ground wheat is represented in the following table, giving the mean of fourteen analyses by Peligot:—

	Mean of 14 analyses.	Extremes Max.	Extremes Min.
Water,	14·0	15·2	13·2
Fat,	1·2	1·9	1·0
Nitrogenous matter insoluble in water,	12·8	19·8	8·1
Soluble nitrogenous matter—albumen,	1·8	2·4	1·4
Soluble non-nitrogenous matter—dextrine,	7·2	10·5	5·4
Starch,	59·7	66·7	55·1
Cellulose,	1·7	2·3	1·4
Ash,	1·6	1·9	1·4

The percentage of ash from the whole wheat is much higher than that of ordinary flour, the bran containing much ash. Thus, 100 parts of bran contain—

	Per cent.
Water,	13·1
Albumen, coagulated,	19·3
Fat,	4·7
Husk and a little starch,	55·6
Ash,	7·3

The analyses of Millon* and Kekulé give the following:—

	Wheat bran. Millon.	Wheat bran. Kekulé.
Starch,	52·0	67·3
Gluten,	14·9	
Sugar,	1·0	...
Fat,	3·6	4·1
Wood fibre,	9·7	9·2
Salts,	5·0	5·6
Water,	13·8	13·8

whilst 100 parts of flour, according to Wanklyn, contain—

	Per cent.
Water,	16·5
Fat,	1·2
Gluten, &c.,	12·0
Starch, &c.,	69·6
Ash,	·7

The nitrogenous matter of the cereals has been usually determined by a combustion and subsequent estimation of the nitrogen. Mr. Church has, however, shown that this method of estimation is not perfectly reliable as a measure of the flesh-formers, or albuminous matters properly so called. In a valuable recent series of researches on this point, with regard to wheat, barley, and oats, Mr. Wigner has shown that these nitrogenous flesh-forming constituents have been over-estimated, since nitrogen combined as nitric acid, nitrous acid, and alkaloids, is present in larger quantities than has been hitherto supposed. This is more especially true as regards the husk and bran, very little non-coagulable nitrogenous matter being contained in the flour properly so called. These analyses were carried out as follows:—

50 grains of the sample were ground in a warm porcelain mortar with enough carbolic acid to form a paste. Two or three drops of dilute acid were added, and the paste then diluted with hot carbolic acid and allowed to cool, filtered, and the filter washed with carbolic acid of the same strength. By this treatment all the true albuminoids were coagulated and remained in the filter, while any nitrogenous matter, either as nitrates, nitrites, alkaloids, or gluten, passed through the filter. The residue in the filter was washed down into the point as far as possible, and the filter dried; the residue detached, and the filter itself finely shredded with scissors and ground to powder, and then burnt in a combustion-tube in the usual way.

The samples were collected so as to give examples of every

* *Comptes Rendus*, t. 28, p. 40.

class of wheat, barley, and oats, and ground by the operator. Treated in this manner, Mr. Wigner found that 17·7 per cent. of the total nitrogen in wheat, 17·6 per cent. of that in oats, and 14·7 per cent. in that of barley, as an average, deduced from the examination of fifteen samples of each, was present in such a form as not to be capable of coagulation by carbolic acid. The extremes in various samples differed widely, and it would appear as though we may have by this process a method of distinguishing the true nutritive value of one sample of grain from another.* In a recent research by the author (still proceeding), the nitrogen as nitrates in the bran was estimated as ·0071 grm. per cent.; an alkaloidal peptone was precipitated by phosphomolybdic acid; and found to exist in the proportion of about ·75 per cent. In whole meal the nitrogen as nitrates was ·043 per cent., the alkaloidal peptone 1·00 per cent.

The nitrogenous constituents of flour comprised under the name of gluten are probably, from the recent researches of T. Weyl and Bischoff,† not ready formed in the flour, but the result of the action of a ferment like myosin, which, however, has not been isolated. This theory would account for the fact that (as observed by Mitscherlich and Krocher) wheat in which no sugar could be found before being sent to the mill, on being moistened and ground yielded as much as 4 per cent. of sugar.

Gluten is composed of at least four bodies—*gluten-caseine, gluten-fibrine, mucedin,* and *gliadin.*

Gluten may be obtained by merely kneading the flour into a paste, and then washing all the starch out of the paste in a thin stream of water. As thus obtained it is, in the moist state, a yellowish-grey, very elastic, adhesive mass; and when dry, somewhat horny. It dissolves for the most part in alkaline liquids and in acetic acid. From the gluten the four bodies mentioned may be separated as follows:—

1. *Gluten-caseine.*—The well-washed gluten is digested a few days with potash solution (for every 100 grms. of gluten about 3 to 4 grms. KHO). The clear solution is decanted from the insoluble residue, and precipitated by acetic acid in the least excess. The precipitate is exhausted successively with 60 per cent. and with 80 per cent. alcohol, then with absolute alcohol, and lastly with ether. The insoluble portion now consists of *gluten-caseine*, which may be purified by solution of weak potash lye, precipitated by acetic acid, washed with water and alcohol, and dried in a vacuum. It forms a whitish-grey, voluminous,

* See *Analyst*, July, August, 1878.

† *Ber. der Deutsch. Chem. Gesellschaft*, 1880, p. 1064.

earthy mass, soluble in dilute alkaline solutions, but insoluble in water, whether hot or cold. At 100°C. it soon changes into a modification insoluble in alkaline fluids. Its solution in very dilute alkaline fluids becomes turbid on exposure to the air, and is precipitated in a flocculent condition by the heavy metals. The elementary analysis of gluten-caseine gives the following percentages :—Carbon 52·9, hydrogen 7·0, nitrogen 17·1, oxygen 22·0, and sulphur 1·0. On heating gluten-caseine with sulphuric acid, tyrosin, leucin, glutamime acid, and asparagic acid with ammonia, are among the products.

The gluten-caseine of rye seems to be similar to that of wheat [*Ritthausen*].

2. *Gluten-fibrine.*—The substances remaining in solution from 1. are gluten-fibrine, mucedin, and gliadin. The first is separated by distilling the united alcoholic extracts to one-half, when it separates as a brownish-yellow mass. It may be purified by repeatedly dissolving in a little 60 to 70 per cent. alcohol, from which it separates on cooling. This property is, indeed, characteristic of gluten-fibrine. It forms a tenacious brownish-yellow mass, becoming horny on drying. It is insoluble in cold water ; boiling water partly decomposes and changes it into a modification insoluble in alcohol, acetic acid, and potash. The elementary composition of gluten-fibrine, according to Ritthausen, is carbon 54·3, hydrogen 7·2, nitrogen 16·9, oxygen 20·6, and sulphur 1·0 ; this points to the formula $C_{37}H_{59}N_{10}O_{11}$.

3. *Mucedin.*—The alcoholic extracts from 2. contain mucedin and gliadin, and are united and evaporated to dryness. The varnish-like residue is treated with ether to remove fat, and dissolved in warm 60 to 70 per cent. alcohol, allowed to cool, and filtered from any gluten-fibrine still remaining. The *mucedin* is now precipitated in a flocculent state by strong alcohol, and by a repetition several times of this operation is obtained pure. When fresh, it is a whitish-yellow, slimy mass ; when dry, a horny, crumbling mass. It dissolves easily in 60 to 70 per cent. alcohol, but is precipitated by 90 per cent. alcohol. The acetic acid solution is coloured a beautiful violet on the addition of sulphate of copper and potash, and slightly warming.

The mucedin from rye and barley is similar to that of wheat [*Ritthausen*]. The elementary composition of mucedin is as follows :—

	Wheat.	Rye.	Barley.
Carbon, ...	54·1	53·6	54·0
Hydrogen, ...	6·9	6·8	7·0
Nitrogen, ...	16·6	16·8	17·0
Oxygen, ...	21·5	22·3	21·3
Sulphur, ...	·9	·5	·7

4. *Gliadin.*—Gliadin is obtained by evaporating the alcoholic solution left from 3. It then remains behind as a clear yellow varnish, which is so tenacious that it may be drawn into threads. By treating it with absolute alcohol and ether, it is changed into a friable, lustreless mass. It is easily dissolved by 40 to 80 per cent. alcohol, and this solution is made milky by absolute alcohol and water, turbid by ether. By boiling it is changed into an insoluble modification. If digested with cold water it dissolves, and the solution is opalescent and frothy, giving a precipitate with tannic acid and soda. Gliadin dissolves in dilute alkaline and alcoholic solutions and in acetic acid; on neutralisation, or on addition of salts of the heavy metals, precipitates are formed. The elementary composition of gliadin is as follows:—

	Mean of two analyses.	
	Ritthausen. Wheat Gliadin.	U. Kreusler. Oat Gliadin.
Carbon,	52·5	52·6
Hydrogen,	6·8	7·6
Nitrogen,	18·4	17·7
Oxygen,	21·5	20·4
Sulphur,	·8	1·7

W. Mayer has discovered a very important ratio between the total phosphoric acid in wheat and corn generally, and the total nitrogen—1 part of phosphoric acid corresponding to 2 parts of nitrogen; the extreme variations do not appear to be more than from 1 : 1·83 to 1 : 2·19. Ritthausen, U. Kreusler, and Pote, have, however, found that in wheats very rich in nitrogen, the proportion may be—phosphoric acid 1· to 1·31.

ANALYSIS OF FLOUR.

§ 84. The analysis of flour should in all cases be preceded by a careful microscopical examination, combined with measurement by a micrometer in order to detect any foreign starches, &c. Flour in this country is pretty well free from organic admixture; but cases do occur, and have occurred in other countries, in which there has been, from carelessness in the cultivation and reaping, some one or other of the following seeds:—*Melampyrum arvense* [Scrophulariaceæ], *Lychnis cithago, Lolumentum temulentum;* or, in bad seasons, "blighted" and "ergotised" corn is ground up with good corn.

The *Melampyrum arvense*, or *purple cow wheat*, is a not uncommon flower in cornfields. Its structure is unlike that of wheat, and may be discovered by the microscope. A chemical test is as

follows:—About 15 grms. of the flour are made into a soft paste with acetic acid, diluted with double its volume of water. The paste is placed in a platinum dish, and the water and acid completely driven off by a gentle heat. The paste on section, should the melampyrum have been mixed with the flour, shows a colouration, violet or purple, according to the quantity.

Quite lately C Hartwich found a rye bread which was of a violet colour. The rye flour from which it was made contained no less than 1·6 per cent. of the seeds of the melampyrum. An alcoholic extract of the flour showed an intense green colour, and sulphuric acid gave a blue play of colours. The seeds not only of *Melampyrum arvense*, but also of *M. cristatum*, *Rhinanthus hirsutus*, *Alectorolophus major* and *minor*, *Euphrasia odontidis*, and *Pedicularis palustris*, all give a violet colour to bread, and probably contain the same colouring-matter—rhinanthin.*

The *Agrostemma*, or *Lychnis cithago*.†—The common corn-cockle of our fields is without doubt poisonous, containing an alkaloid, "*saponin*." Flour mixed with seeds of the lychnis has a disagreeable bitter taste, and the foreign substance may be discovered by a microscopical examination. On treating the flour with ether, the percentage of oil is much increased; the oil extracted by ether is also of a strong yellow colour, and acrid.

In cases where a microscopical examination has discovered the seeds of agrostemma, A. Peterman‡ has recommended the separation of saponin. 100 grms. of the flour are exhausted by a litre of 80 per cent. alcohol, and filtered hot; the filtrate is precipitated by absolute alcohol, the precipitate separated and dried at 100°, and then exhausted with cold water. This extract is again precipitated with absolute alcohol, and the saponin obtained as a yellowish powder of sharp burning taste. Saponin is easily soluble in water, and is perhaps best recognised by its power of communicating a soapy appearance to water. Water containing 1000th of its weight of saponin froths on shaking just like a solution of soap. Concentrated sulphuric acid dissolves saponin with, first, a red-yellow colour, changing into violet, and later, into a more intense red. The watery solution is precipitated by acetate of lead, and, if concentrated, by baryta water. 2 grms. given to an adult will cause physiological symptoms, mainly consisting of nausea, diaphoresis, and diuresis;

* *Archiv. der Pharmacie*, 217, p. 280.

† The plant belongs to the nat. order *Caryophyllaceæ*, or clove-worts: the flower is large and purple; the stem dichotomous, from 2 to 3 feet high; the calix is coriaceous, ribbed, with 5 linear lanceolate, constantly erect, patent, very long segments, styles downy, capsula 5-toothed.

‡ *Ann. de chimie et de pharmacie*, 5. xix., p. 243.

·5 grm. is a fatal dose for a kitten; the fatal dose for a human adult is not known.

The *Lolium temulentum*, or *Darnel*, has rather frequently been found as an impurity in flour.

If flour contain darnel it may be detected by the characters of the alcoholic extract. The flour is digested in alcohol of 35°; if it is pure, the alcohol remains perfectly clear and limpid, or at the most, takes a very pale straw colour, from dissolving a little colouring-matter in the envelopes of the wheat, which may be in the flour, nor is the taste disagreeable. If, on the contrary, it contains darnel, the alcohol takes a greenish hue, which darkens gradually. The taste of the alcohol is acrid and nauseous, and on evaporation it leaves a yellowish-green resin.

Detection of Ergot in Flour.—It is most important to examine flour for grain matters damaged by mould, and especially ergot. A good preliminary test is that recommended by A. Vogel.* The flour is stained with aniline violet, and then examined microscopically: the damaged starch granules take up the colour intensely. This staining will take place with flour damaged by any fungus, and is not a special test for ergot. The best chemical method is that of Jacopy, as modified by J. Petri.† 20 grms. of the flour are placed in a proper exhausting apparatus, such as is described at page 68, and exhausted with boiling alcohol until the last alcohol is colourless. To the alcoholic solution 20 drops of cold diluted sulphuric acid are added, and the liquid is filtered and examined by the spectroscope in thinner or thicker layers, according to the depth of colour. If the flour is ergotised, the alcoholic solution will be more or less red, and show two absorption-bands in very dilute solution, one lying in the green near *e*, and a broader and stronger band in the blue between *f* and *g* On mixing the original solution with twice its volume of water, and shaking successive portions of this liquid with ether, amyl-alcohol, benzine, and chloroform, the red colour, if derived from ergot, will impart its colour to each and all of these solvents. Other tests have been proposed from time to time; as, for example, a yellow colour developed when flour is treated with an alkaline solution, and the development of a smell of trimethylamine when the potash solution is heated. It may, however, be remarked that the yellow colour would not be conclusive as to the presence of ergot, for otherwise damaged flour will show this reaction; and as for the smell of trimethylamine, it may be noticed when certain gummy matters are decomposing, and though a flour producing such an odour with potash cannot be considered healthy,

* *Chem. Centralblatt.* [3 f.] 10. 559.
† *Zeitschrift für Anal. Chem.* 1879, pp. 211-220.

the odour in itself would not be conclusive in regard to the presence of ergot. The presence of ergot, and of the seeds mentioned, must be regarded, not as adulterations in the sense of a fraudulent addition, but as impurities. Nevertheless, an analyst would naturally certify, under the "Sale of Food and Drugs Act," if flour sold as good flour should be found to contain any of these substances.

The following substances have been fraudulently added to wheaten flour:—Rye, rice-meal, barley-meal, potato starch, the flour from various Leguminosæ, linseed-meal, buckwheat, and some other starches. It may once again be said, that in England all these adulterations of flour are of extreme rarity (with, perhaps, the exception of potato flour and ground rice); but there is good evidence that in times of scarcity, with bread at famine prices, all kinds of substances have been mixed with flour and sold. What has happened may occur again, and it is therefore well to know the chief chemical tests which have been recommended to detect even these uncommon admixtures. The general test recommended by A. E. Vogel may be useful: The suspected flour is extracted with 70 per cent. alcohol, to which hydrochloric acid has been added, in the proportion of 5 per cent. of the alcohol employed. If the flour is made of either pure wheat or rye, the alcohol remains colourless; it is of a pale yellow if either barley or oats should be present; orange-yellow with pea flour; purple-red with mildewed wheat; and blood-red with ergotised wheat.

Potato Starch.—So long ago as 1847, M. Donné proposed an excellent test for potato starch in wheat flour. The flour is examined in a very thin layer under the microscope, in the ordinary way, and then, while it is under observation, a weak solution of potash is added, when potato starch will begin to swell, and reach four or five times its volume, while wheat starch is scarcely affected. The test is best applied by putting a little of the flour on a stage micrometer; it is then easier to appreciate the alteration in size of any particular starch. When this method of detecting potato starch is combined with the subsidence process, proposed by Lecanu in 1849, so small a quantity as one part of potato starch in a thousand of wheat flour may be detected. The subsidence process is as follows: Any convenient quantity of flour, say 100 grms., is treated with 40 per cent. of its weight of water, and the gluten separated in the usual way; the washing water is well stirred, and passed through a sieve to retain the larger suspended matters, and then allowed to rest in a conical vessel until a deposit has formed. Without waiting for the supernatant water to become clear, it is decanted, and the

deposit mixed by stirring with more water, and allowed again to deposit for a short time. The water is decanted, and the process again gone through. By this means the final and lowest deposit will consist almost entirely of potato starch, which, being of greater specific gravity than wheat, always subsides first. M. Robine, curiously enough, relies more upon a chemical identification of the apex of the cone of deposit than upon a microscopical, which latter is so much more decisive. The last deposit is recommended to be received on a lump of dry plaster, the apex cut off and triturated in an agate mortar—glass, porcelain, and Wedgwood mortars do not answer—and tested with iodine, which gives a blue colour with potato starch; but under these circumstances, not with wheat starch, the friction of the smooth agate not having been sufficient to tear the envelopes off the latter. M. Chevallier has also recommended a method for the detection of potato starch, based on the resistance which the wheat granules possess to the destruction of the outer membrane. Equal weights of flour and sand are to be triturated with water until a homogeneous paste is formed, which is then diluted and filtered; to the filtrate is added a freshly-prepared solution of iodine, made by digesting for about ten minutes 3 grms. of iodine in 60 cc. of water, and then decanting. If the flour is pure, this addition will give a pink colour, gradually disappearing; whilst if potato starch should be present, the colour is of a dark purple, only disappearing gradually; by comparing the reaction with flour known to be pure, this difference of behaviour is readily appreciated.

Detection of Leguminous Starches, &c.—As previously stated, the leguminous starches give no play of colours when examined by polarised light and a selenite plate, and are thus easily detected among the iridescent wheat starches. By treating the flour also under the microscope with a solution of from 10 to 12 per cent. of potash, it is possible to dissolve the starch granules of the leguminous plants, and leave a characteristic reticular tissue, made up, for the most part, of irregular hexagons. The addition of lentils or vetches, on account of the brown colour of the seeds, can only take place in minute quantity, and then could only be added to dark flours of inferior quality.

Bean flour, haricot flour, or pea flour, may be mixed up to 5 per cent. without imparting any particular appearance, odour, or taste. Beyond that, all these characters are altered. Bean flour is said to give to the crust a more golden brown, which is agreeable to the eye. There is a principle in beans and vetches which, treated with nitric acid and ammonia, gives a red colour. The method to separate this colouring-matter from falsified flour is

to exhaust any convenient quantity with boiling alcohol, and to evaporate the alcohol to a syrup. This syrup is freed from fatty matters by ether, and the insoluble residue exposed successively to the vapours of nitric acid and ammonia. An amaranth red colour denotes the presence of these substances. M. Biot has, however, stated that wheat from the Caucasus responds to this test although perfectly pure, so that, like many other reactions, it must not in itself be taken as conclusive. M. Marten proposed to separate *legumin*, and M. J. Lemenant des Chenais has modified Marten's original process as follows:—The gluten is separated in the usual manner, and to the liquid containing the starchy matters is added ammonia, which is a good solvent of legumin. The starch is allowed to deposit, the liquid is filtered, and to the filtrate a very dilute mineral acid is added, which precipitates legumin if present. The legumin is filtered, collected, dried, and weighed. According to M. Lemenant des Chenais, ·9 of legumin in 100 grms. of flour represents an adulteration of 5 per cent.

The most scientific process, which embraces a fairly complete examination of flour for the leguminous constituents, is that of Lecanu:—The gluten is first separated in the usual way. The washing water, containing starch, soluble matters, and legumin, if present, is passed through a sieve to separate coarse particles in suspension, and then diluted sufficiently and allowed to deposit. The liquid is divided into two parts, and one part is allowed to putrefy or ferment spontaneously. With pure flours the lactic acid fermentation is most common; with flours containing legumin there is a putrid fermentation. The other portion is, after decantation and filtration, concentrated until a yellowish scum forms on the surface; it is allowed to cool, and separated from the albumen which all flours contain. Then legumin is precipitated by adding drop by drop acetic acid. Legumin is identified by its properties. It is without colour, taste, or odour. When dried it is of a horny consistence, insoluble in alcohol, not coloured by iodine, but very soluble in potash or ammonia water, from which solution it may be precipitated by the addition of an acid. The deposit is submitted to a careful microscopical examination, and tested with iodine to colour the starch and leave uncoloured the cellular tissue, or with potash in the way described on page 156. The suspended particles on the sieve are also examined microscopically, because they often contain large fragments of leguminous cellular tissue.

The leguminous starches contain more mineral matter than wheat flour—for example, pea flour contains, on an average, 2·65 per cent. of ash; flour, ·7. It hence follows that if pea flour be

mixed with wheat flour in the proportion of 10 per cent., the ash would be ·87 instead of ·7, and it has been proposed to make this a test of the presence of such foreign starches; but, as the example just given shows, with moderate adulteration it would not be at all conclusive, and must only be considered one of the auxiliary means.

M. Rodiguez has ascertained that when pure flour is submitted to dry distillation in a stone retort, and the distillate is collected in a vessel containing water, the latter will remain perfectly neutral. But if bean, pulse, or pea meal has been added, the water will have an alkaline reaction. This test appears of doubtful value; for, provided the distillate is alkaline, the alkalinity may, it is evident, have arisen from a variety of causes besides the addition of the substances mentioned. It has also been shown by Bussy that certain cereals yield on distillation an acid product.

Lassaigne (taking advantage of the fact that haricot beans, as well as beans, contain a tannin in their envelopes) adds a salt of iron, which, with pure flour, gives a feeble straw colour, but mixed with either of the two mentioned, or, of course, with any substance containing tannin, gives various shades, from orange-yellow to very dark green.

§ 85. *Detection of Alum and Mineral Matters generally in Flour.*—The most important test for the detection of mineral substances generally in flour is, without doubt, what is known as the "chloroform" test—a test which, it would appear, was first proposed by M. Cailletet, a pharmacist of Charleville, in 1869, and was in England brought prominently before the notice of analysts by the researches of Dr. Dupré. The principle of the method is simple and obvious. The chloroform is of sufficient gravity to float the starchy substances and allow the alum, sand, sulphate of lime, or other mineral matters, to sink to the bottom. It, besides, has no very appreciable solvent action on alum, and none at all on the generality of mineral or saline substances. No solution made of sufficient specific gravity, by dissolving salts in water, or any other means, will answer the same purpose as chloroform, because, directly the flour is moistened with water, the alum is decomposed by the phosphate of potash present in the flour, and also forms an insoluble compound with the gluten; and, under those circumstances, as alum, it is impossible to recover the alumina.* The method is as follows:—The tube figured in the article on "Beer" is taken, and a weighed quantity of the flour, from a quarter to half a pound, is placed in it, and sufficient methylated chloroform added to form a thin sort of paste; the

* This is the orthodox doctrine, but the latest researches of the author do not wholly confirm the view stated in the text (*see Index*).

cylinder is closed by a stopper, shaken up once or twice, and allowed to stand over night. The next morning the "rod-stopper" is inserted and the cap removed; the latter will contain sand from the millstones, sulphate of lime, alum, or any other mineral powder of a greater specific gravity than chloroform, that happened to be in the flour; this fluid is placed in a burette, some more chloroform is added, and the matters allowed again to subside; lastly, the powder, with a little of the chloroform, is drawn off into a watch-glass, the chloroform evaporated, and the powder digested in warm water, filtered into a clean watch-glass, and allowed to evaporate spontaneously. If alum were present crystals will be obtained, easily identified by their form, and these, if necessary, can be produced in court as a "*corpus delicti*." The chloroform which has been used may be in a great measure recovered by simple filtration, then purified by distillation in the usual way.

The alum crystals may be easily identified by their form under the microscope, and by the reaction with gelatine and log-wood. It may be a matter of some importance to be able to say whether the alum present is a potash or ammonia alum. The best method of detecting this is to take the smallest crystal, and having previously dropped a single drop of Nessler solution on a porcelain slab, stir the crystal into the Nessler; an immediate brown colour and precipitate is produced if the alum was an ammonia alum. Dr. Dupré has made some experiments as to the amount of alum which by this process it is possible to recover. Three mixtures were made, containing respectively 28, 10, and 2 grains of very finely powdered ammonia alum in 100 grains of a pure flour. On separation of the alum by the chloroform test, the residue or deposit obtained from the chloroform was dissolved in cold water, and precipitated by baric chloride, and the sulphate of baryta obtained calculated into ammonia alum; the result was that 27·1, 8·21, and 1·14 grains of alum were respectively recovered, instead of 28, 10, and 2 grains, which must be considered as fairly satisfactory. The sand and silica obtained by the chloroform process will be filtered off, and should be dried and weighed, more especially since there has been found to be a relationship between the silica present and the alumina in flour not existing as alum, but as clay, &c.

The Logwood Test.—A freshly-prepared tincture of logwood becomes blue when alum and certain other salts are added to it; an excellent and readily applied test has been proposed based on this reaction. To apply the test to flour, the following is the usual process:—

Fifty grms. of flour are weighed out and mixed by the aid of

a glass rod with 50 cc. of distilled water; to this is added 5 cc. of recently prepared logwood solution, alkalised by 5 cc. of solution of ammonium carbonate. If $\frac{1}{10000}$ part of alum is present, the flour will become of a lavender-blue colour instead of pink. An approximate estimate of the quantity may be obtained by having a standard solution of pure alum, 1 grm. to the litre, and adding known quantities to exactly similar emulsions of pure flour, and testing as before with logwood, until an emulsion is obtained of very similar hue to the flour originally tested. If the cold extract gives a blue tint with the logwood test, or if the flour be submitted to dialysis, and the diffusate responds, alum is present as alum, and is not derived from dirt, clay, or from the millstones themselves.* The author now uses little strips of gelatine to concentrate the alum on: a bit of gelatine is soaked in the cold extract of the suspected flour for 12 hours, it is then taken out and steeped in the ammoniacal logwood; if alum is present the gelatine becomes of a beautiful blue colour;† the test is much more decided than as applied in the usual way. The same blue colour is produced by the presence of magnesia, and clayey matters may also cause a bluish tint. Nevertheless, if a flour or bread does not respond to this test, it is certain that alum in any quantity is not present; on the other hand, if a blue colour is produced, there is certain to be either an adulteration with alum or some other admixture, and the sample should be more thoroughly examined.

Hermann W. Vogel‡ has shown that alum and magnesia salts can be recognised by their influence on the spectrum of purpurine. It is evident that here is a process by which the analyst may be assisted in his diagnosis of the cause of any blue colour imparted to flour. Pure purpurine gives, in saturated solutions, a spectrum extinguishing wholly the blue part. An alcoholic solution diluted until it is of a straw-yellow colour extinguishes the blue only partially, and shows two marked absorption-bands at F and *b* E. (see fig. 12.) A diluted watery solution does not show these absorption-bands, but instead there appears a stronger absorption in the green between F and *b*, a weaker in the yellow from E. This reaction is dependent on a trace of alkali, for it is intensified by ammonia, whilst a slight excess of acetic acid colours the fluid yellow, and then there is only a weak absorption. The

* The millstones are sometimes mended with an alum cement. This circumstance will of course, from time to time, be utilised for purposes of defence.

† The author, while these sheets are passing through the press, is developing the test mentioned by further research, and a note will be added giving his final results at the end of this volume (*see Index*).

‡ *Ueber eine empfindliche Spectral Analytische Reaction auf Thonerde und Magnesia.*

solution of purpurine should be prepared from purpurine which has been purified by sublimation, and it should be made very feebly alkaline. To test for alum it is best to take the deposit from the chloroform process already described, and dissolve it in not more than 1 cc. of water. 2 cc. of water are now placed either in a test-tube or a little glass cell, and three drops of a saturated alcoholic solution of purpurine added, and then alkalised by a drop of fourfold diluted ammonia water. On observing this solution by the spectroscope, it appears as curve No. 12, fig. 12. A drop of the alum solution is next added: in dilute solutions two bands gradually appear; in the presence of half a milligramme of alum, the bands appear after the lapse of several minutes. Magnesia presents similar appearances, but is at once distinguished from alum by the fact that the bands are destroyed by the addition of acetic acid.

Proximate Analysis of Flour.

§ 86. The constituents of flour to be determined are—

(1.) Water.
(2.) Fat.
(3.) Cold Water Extract. { Sugar, Gum, and Dextrine. Vegetable Albumen. Phosphate of Potash.
(4.) Gluten.
(5.) Ash.

(1.) The *water* is taken in the ordinary way; that is, by weighing carefully about 1 to 3 grms. in a tared dish, and exposing it to the heat of the water-bath until it ceases to lose weight.

(2.) The *fat*, according to the researches of Peligot, must be determined in the *perfectly dry* flour, error resulting in any other case.

(3.) The *cold extract* is obtained by digesting 10 grms. of flour in 500 cc. of water, and filtering and evaporating down 250 cc. in a platinum dish. According to Wanklyn, 100 grms. of flour yield to water—

	Grms.
Sugar, gum, and dextrine,	3·33
Vegetable albumen,	0·92
Phosphate of potash,	0·44
	4·69

On igniting the extract, the ash should consist entirely of phosphate of potash. When the weight of the ash is known, it may be dissolved in water, and the quantity of phosphoric acid

estimated by titration with uranium solution; and if from this there is any discrepancy between the calculated phosphate of potash and that found, the ash should be carefully examined.

The determination of the sugar and dextrine may be made by the processes described at p. 113 *et seq.*; but it is usually sufficient to obtain merely the weight of the cold extract and the weight of its ash.

A method of estimating the value of flour by the amount of solid matter dissolved by acetic acid has been proposed by M. Robiné, who has taken advantage of the property which acetic acid, when properly diluted, has of dissolving the gluten and albumen, and leaving intact the starchy matters. The acetic acid solution increases in density according to the amount of solid substances it dissolves, and he has constructed an areometer, graduated in such a manner that each degree represents the value of the flour expressed in a loaf of 2 kilometres weight. A table is sold with the instrument, and without doubt, although not exact enough for the food-analyst, the process is of some value to the buyer of flour. The areometer is called "*Appréciateur des Farines.*" The acetic acid is diluted until the "*appréciateur*" sinks to 93° on the scale. 24 grms. of flour of the first quality are taken for the assay, but if the flour is of the second quality, then 32 are taken. This quantity of flour is washed successively with six quantities of the acid, each time using 31·25 cc., and all the time triturating in a mortar. After ten minutes the whole is poured into a vessel, plunged in cold water of exactly 15°, and allowed to remain at rest for an hour; the liquid is then decanted, and the "*appréciateur*" floated in it. By the number indicated, the number of loaves of bread 2 kilogrammes in weight which 150 kilogrammes of the flour will give is at once seen.

(4.) *The gluten or albuminoids* can only be approximately determined by the washing process described at page 150; the usual method is to make a careful combustion of a small weighed portion of the flour with cupric oxide, and to measure the nitrogen obtained, and then to multiply the percentage of nitrogen found by the factor, 6·33.

(5.) *The ash* is burnt in the usual way, and is somewhat difficult to consume, especially if any quantity of flour is taken. It has been proposed to mix the flour with nitrate of ammonia, then to heat carefully, and directly fusion commences, to withdraw the flame. Flour can certainly be burnt up very quickly in this way. If this method should be adopted, it will be very necessary for the analyst to ignite a corresponding quantity of nitrate of ammonia in a platinum dish, and see whether any

residue is left. Occasionally, nitrate of ammonia may be met with which is sufficiently impure to cause an error in analysis. Flour may also be burnt up in a platinum trough in a combustion tube. In this case it is most convenient to begin the combustion in ordinary air, and then to finish in oxygen. A properly burnt flour ash should be below 1 per cent.; if it attains 1 per cent., mineral adulteration is probably present. (The method of estimating alumina and silica in the ash of flour is fully detailed at pages 169-171, and also the relationship between the silica and the alumina.)

Legal Case Relative to Flour.

§ 87. The following brief abstract will show the lines of defence likely to be adopted :—

In the month of February, 1880, the case of a miller summoned for selling adulterated flour was heard at the Eckington sessions. The analyst deposed to having found alum, in the proportion of 24 grains to 4 pounds of flour. He obtained the alum as alum by the chloroform process. He shook the flour with chloroform, which was a heavy liquid, the flour floated, and the alum sank to the bottom; it was from what sank that he obtained crystals in the characteristic form of alum; he tasted it, and it had the astringent taste of alum. It gave the logwood reaction such as alum gives. He placed about 30 grains of the flour in the chloroform, and the precipitate was probably one-eighth of a grain. He let the chloroform evaporate, and so obtained the crystals; alum crystallises in octohedra of the cubical system; the alum was in the fragmentary form until water was added to the deposit from the chloroform, and the liquid filtered and evaporated. Silica crystallised in hexagonal prisms, and could not be mistaken for alum, besides, it was insoluble in water. He had made an analysis for the purpose of estimating the quantity of alumina present, and found it was in the proportion corresponding to 30 grains of alum to 4 pounds of flour. On being asked whether clay and dirt might not account for the alumina, the answer was that clay and dirt might be present as a silicate of alumina, but it would be insoluble in water, and would not give the reaction with logwood. The defence was—

1. That the analyst was mistaken.

2. That alum was occasionally used in the mill for filling up the cracks in the stones.

3. That the defendant had made his flour lately from foreign grain on account of the bad quality of English wheat at the time, and there was nothing astonishing in finding 24 grains of alum in such wheat although perfectly pure and unadulterated.

An analyst was called for the defence who did not seem to be acquainted with the chloroform test, but had estimated the total alumina. The gist of his evidence was that he could not say positively whether there was alum or not in the flour, and that he thought that so small a quantity of alum as could be separated from 30 grains could not be identified. The matter was then referred to Somerset House, and the Government chemists fully confirmed the presence of alum in the flour.*

* *Analyst*, 1880, p. 72-86.

BREAD.

§ 88. The term Bread has been applied to any form of flour made into bread, but that made from wheaten flour can alone be treated of here. Wheaten bread is the flour of wheat made into a paste with water, and the paste is permeated by carbon dioxide, either by adding yeast, which causes a true fermentation with the production of alcohol and carbon dioxide, or the carbon dioxide is added in solution in water to the paste, as in Dauglish's system. The explanation of the bread-making process is not thoroughly worked out in all its details, but the following theory agrees fairly well with what is witnessed: On adding yeast to the dough, it is placed on one side, at a suitable temperature, and allowed to rise, that is, fermentation proceeds, and there is a continual evolution of gas; the starch in some degree becomes changed into sugar, which sugar is decomposed into carbon dioxide and alcohol. The gluten prevents, or rather retards, the escape of the carbon dioxide, and the tension of the warm gas expands little cells, and gives to the bread its familiar light spongy appearance. The alcohol mostly escapes, and although in large bread-making establishments it would seem to be feasible and economical to recover the alcohol, hitherto no really good appliance has been invented for this purpose, the apparatuses which have been tried interfering with the baking of good bread. The outside of the loaf, when placed in the oven, is raised to a temperature of from 210° to 212°, but the crumb is seldom much above 100°. The crust is to some extent caramelised, and, on analysis, shows, as might be expected, very much less water than the crumb. Thus, Rivot found in twenty-one samples of bread from 20·45 to 47·11 per cent. hygroscopic water in the crumb, and 16·40 to 27·44 per cent. in the crust. Tracing one by one the chief chemical changes which the flour undergoes under the influence of the yeast-fermentation and subsequent baking, we consider,

1. *Nitrogenous Matters.*—The soluble albumen becomes insoluble, and can no longer be separated from the starch. The gluten-caseine and gluten-fibrine form some intimate combination with the starch. The gliadin, however, still may be extracted out of the bread, as out of the flour, by the action of alcohol. In the crust there is a partial destruction of the nitrogenous substance. Thus, V. Bibra found—

	Wheaten Bread. Nitrogen per cent.	Rye Bread. Nitrogen per cent.
Crumb,	1·498	1·476
Crust,	1·363	1·293

2. *The Starch*, as already explained, is in part changed into sugar, which sugar is further decomposed into carbon dioxide and alcohol; a part of the alcohol appearing as acetic acid, and a part of the sugar appearing as lactic acid. There are also other volatile acids of the acetic series formed (notably with dirty breads), and small quantities of butyric acid can be obtained and identified if the watery extract (which, by the way, always reacts acid) is distilled after the manner of Duclaux. All the sugar formed is not decomposed, but the bread invariably contains more sugar than the flour from which it was made. A portion of the starch is also changed into dextrine, and through all these causes the bread contains always more soluble carbohydrates than the flour.

3. *The Fatty Matters* are not, so far as is known, changed.

4. *The Ash* is not changed, save by the minute proportion of yeast ash which is added to it, an addition quite inappreciable. Further, any salt added by the baker increases a little its weight; but the ordinary method of burning bread volatilises very effectually chlorides of the alkalies, so that the ash of bread is still very small. It has been said that the alcohol escapes, which is true with regard to the bulk of the alcohol. Alcohol, however, has a wonderful property of adhering to organic substances, and Th. Bolas has shown that it can be detected in fresh bread in greater quantities than would *à priori* have been suspected. Thus, he found in six fresh samples of bread the following percentages of alcohol:

Minimum,	·221
Maximum,	·399
Mean,	·313

In two of the samples a week old, he was able to detect ·132 to ·120 per cent. respectively. On keeping bread, there is a continual loss of water, and it becomes "stale" from some peculiar molecular change. That this staleness is not due to the loss of water is proved by the simple experiment of re-baking a loaf, when it becomes for the time fresh again, but more rapidly after this process becomes stale and is notably drier. V. Bibra found that a bread cannot be made fresh again if it has lost 30 per cent. of water, but if the loss of water is below that, it then may be freshened by re-baking. V. Bibra found that wheaten bread lost the following percentages of water:—

After 1 day.	3 days.	7 days.	15 days.	30 days.
7·71	8·86	14·05	17·84	18·48

The mean composition of wheaten bread, from a large number of analyses collected by König, is as follows:—

	Minimum.	Maximum.	Mean for Fine bread.	Mean for Coarse bread.
Water,	26·39	47·90	38·51	41·02
Nitrogenous substances,	4·81	8·69	6·82	6·23
Fat,	·10	1·00	·77	·22
Sugar,	·82	4·47	2·37	2·13
Carbo-hydrates,	38·93	62·98	49·97	48·69
Woody fibre,	·33	·90	·38	·62
Ash,	·84	1·40	1·18	1·09

The ash of a properly burnt wheaten-flour loaf seldom exceeds 1·5 per cent. unless adulterated; anything beyond 2 per cent. would be certainly suspicious of a mineral addition. There has recently been an agitation on behalf of "whole meal bread," and analyses of the greater richness of such bread in azotised constituents are frequently quoted; but such a question cannot be decided by chemical analysis, or, at all events, by ordinary analysis, in which a few constituents are alone estimated. The question is rather a physiologico-chemical inquiry, and the proper way to solve the problem is to go on the lines of the well-known experiments of G. Meyer. A healthy individual is taken and fed on known weights of the substance experimented upon, and the amount of undigested substance recovered from the fæces is weighed. Meyer thus experimented on—

(1.) Horsford-Liebig bread, which is made without the addition of yeast or leaven, the carbon dioxide being developed by the action of bicarbonate of soda on phosphate of potash.

(2.) Munich rye bread, prepared from rye bread and coarse wheat meal and leaven.

(3.) White wheaten bread.

(4.) North German black bread (*Pumpernickel*) prepared out of whole rye meal, and with the use of leaven.

The amount of dry substance, &c., absorbed in percentages of these different breads, was found to be as follows:—

	Dry Substance.	Nitrogen.	Ash.
1. The Black Bread,	80·7	57·7	3·4
2. Horsford-Liebig Bread,	88·5	67·6	61·9
3. Rye Bread,	89·9	77·8	69·5
4. White Bread,	94·4	80·1	69·8

It is thus shown that of the black bread a person would have to eat very much more than of white bread. The white wheaten bread was nearly all absorbed. That this experiment was not made with whole wheaten meal is true, but it still unmistakably casts some doubt on the question as to whether whole meal would be more nourishing than pure white flour.

Alterations of Bread by Moulds, &c.—Red, green, orange, and black spots occasionally appear on bread, and there are several

instances on record of great damage and loss from such parasitic diseases.

In 1856, in France, M. Poggiale was commissioned to examine 22,000 rations served out to the French troops, the bread of which had turned a bluish-black. The bread had been made of inferior grain, but it also contained an enormous number of bacteria. Rather frequently, also, bread and other foods have been attacked by an orange-red growth, which has been attributed to a fungus, to which has been given the popular name of the *red-bread fungus*, its scientific appellation being *Oidium aurantiacum*. A red algæ sometimes appears on bread; it has been named the *Palmella prodigiosa*, and has been specially studied by Dr. Antoine Franchini, of Bologna. To the eye, the algæ resembles almost exactly drops of blood. It is composed of cells and filaments filled with a bright red colouring-matter, which would well repay examination.

The more common moulds of bread are the whitish *Mucor mucedo*, the green *Aspergillus glaucus*, and the black *Rhizopus nigricans*. It has not yet been established that any of the moulds or growths enumerated are in themselves injurious to health; but, as may be expected, they damage the bread, making it deficient in nourishment, and unpalatable.

§ 89. *Adulterations of Bread.*—The adulterations of bread enumerated by writers are sufficiently numerous, but those actually proved to exist are but few. Among organic additions rice flour, potatoes, bean flour, and pea flour are usually given; among mineral, alum, borax, sulphate of copper, sulphate of zinc, chalk, and carbonate of magnesia.

In 1843 and 1847, some bakers in Belgium were convicted of adding sulphate of copper to their bread, and this fraud has been repeated a few years ago by a baker of Calais. There is, however, no reason to believe that English bakers are addicted to these practices, and, as a fact, no conviction has been obtained save for the use of alum. The detection of rice flour, bean flour, foreign seeds is to be undertaken in the same way as described in the sections on flour, save that here the chemical tests are more useful than the microscopical. It is an extremely difficult thing to detect and identify most starches when they have been swollen by heat and altered by fermentation. The only feasible course appears to be to make bread of flour adulterated with the substance suspected to be present, and examine sections and washings of such bread side by side with similar sections and washings of the suspected bread.*

* An exception may, perhaps, be made to this statement in the case of potato starch, which may be recognised tolerably easily even in bread.

§ 90. *Alum in Bread.*—Alum is added to bad or slightly damaged flour by both the miller and the baker. Its action, according to Liebig, is to render insoluble gluten which has been made soluble by acetic or lactic acids developed in damp flour, and it hence stops the undue conversion of starch into dextrine or sugar.

The influence of alum on health, in the small quantities in which it is usually added to bread, is very problematical, and rests upon theory more than observation. But notwithstanding the obscurity as to its action on the economy, there can be no difference of opinion that it is a serious adulteration, and not to be permitted.

In searching for alum, the crust and the crumb should be analysed separately; for many bakers use for the latter a flour technically called "cones," which is strongly alumed, and prepared from a fine species of wheat grown in the south of Europe, mixed with rice. This mixture is used for dusting the kneading trough and kneading boards; in point of fact, for "*facing*" the sponge previous to baking it. To search for alum in the crust, there is no other method save burning to an ash, as shortly to be described; but with regard to the crumb of bread, the *qualitative* test is the same as for flour—viz., an ammoniacal tincture of logwood. From 300 to 400 grains of bread are crumbled in distilled water, and a slip of pure gelatine added, and the whole allowed to soak for twelve hours. On dissolving the gelatine in a little logwood, to which its own volume of a ten per cent. solution of ammonium carbonate has been added, if the bread is pure the solution will be reddish-pink; if the bread is alumed, the solution will be blue, and exhibit the spectroscopic appearances described in the note at the end of this volume (*see Index*). This blue colour is not absolutely decisive of alum, for bread adulterated with magnesia carbonate exhibits the same reaction; but if such a colour is produced, the bread requires further examination.

The author, in some special researches, has recently discovered that a certain portion of alum may always be washed out of bread as alum. He employs the following process: the bread is soaked in water for at least twenty-four hours (about 2 litres of water are used to 100 grms. of bread). The bread is separated by means of a sieve, and the mass afterwards pressed in a cloth, ultimate clear filtration being obtained when necessary by aid of the mercury pump. This extract may be concentrated in a platinum dish, and when cooled a slip of gelatine allowed to steep in a portion over night. The gelatine on being stained with logwood will exhibit a blue colour, if magnesia or alum is present. Another portion of the extract is dried and

burnt up in the usual way, as in the process to be described, and the phosphate of alumina separated. The phosphate of alumina is now fused with sodic sulphate, the result of the fusion being sodic phosphate and alumina. The sodic phosphate is washed out with water; the alumina boiled with a drop or so of dilute sulphuric; and to the sulphate of alumina thus obtained, a little solution of ammonia is added, and the whole put in a watch-glass to crystallise over sulphuric acid. To obtain crystals in this way is often very difficult, but that alum is really present can be readily proved by the reactions of the solution with reagents. By strictly following these directions, a very small quantity of alum can be detected. In a test experiment in a sample of bread in which 5 grains of alum had been added, it was found possible to obtain 1·5 in aqueous solution.

The *quantitative* method for estimation of the *total alumina* in bread, as originally proposed by Dupré, and slightly modified by Wanklyn, is as follows:—100 grms. of bread are incinerated in a platinum dish, until the ash does not exceed 2 grms. in weight. The ash is then moistened with 3 cc. of pure strong hydrochloric acid, and 20 to 30 cc. of distilled water added; the whole is boiled, filtered, and the precipitate (consisting of unburnt carbon and silica) well washed, dried, burnt, and weighed. To the filtrate containing the phosphates, 5 cc. of strong solution of ammonia are added. If the bread has been alumed, the phosphates now precipitated are those of lime, magnesia, iron, and alumina, of which the latter (viz., phosphate of iron and alumina) are insoluble in acetic acid, so that their separation is easy. The liquid is *strongly acidified* with acetic acid, boiled and filtered, and the phosphates of alumina and iron washed and weighed. Unless the liquid has been acidified sufficiently, phosphate of lime contaminates the precipitate and vitiates the results, so that this is an essential point. The last step is resolution of the precipitate in acid, and the estimation of the iron; this is usually best effected by a colorimetric process. A standard solution of metallic iron is made by dissolving a gramme of fine iron wire in nitro-hydrochloric acid, precipitating with ammonia, washing the peroxide of iron, and dissolving it in a little hydrochloric acid, and diluting accurately to 1 litre [1 cc. = 1 mgrm. of metallic iron]. On now adding to an unknown very dilute solution of iron a known quantity of strong ammon. sulphide, a certain colour is produced, and this colour is exactly imitated in the usual way by a similar quantity of ammon. sulphide and the standard solution, the whole operation being conducted on the well-known principles of colorimetric estimation. The amount of iron in the precipitate being known,

it is calculated into phosphate, and the phosphate of iron subtracted from the total weight of the precipitate gives the weight of the phosphate of alumina. From Mr. Wanklyn's experiments it would seem that in the case of bread ash, it is unnecessary to evaporate the hydrochloric solution to dryness, as is usually done, and that the separation of silica is complete by the method just detailed.

Another perfectly valid way of estimating alumina in bread or flour, consists in a modification of the old Normandy process. The bread is burnt up as before, the ash powdered and treated with hydric chloride, diluted with water, boiled, and filtered. The filtered solution is again boiled, and whilst boiling poured into a very strong solution of sodic hydrate, the whole boiled, filtered, and washed. To the filtrate is added a few drops of disodic phosphate, it is then slightly acidified with hydric chloride, and subsequently rendered just alkaline by ammonia. The precipitate is collected, washed, and weighed as alumina phosphate.

The following table will be of use in the conversion of phosphate of alumina into alum :—

Phosphate of Alumina, Al_2O_3,PO_5. Parts.		Ammonia Alum, $NH_4,Al.2SO_4.12H_2O$. Parts.	Potash Alum, $KAl,2SO_4,12H_2O$ Parts.
1	=	3·733	4·481
2	=	7·466	8·962
3	=	11·199	14·443
4	=	14·932	17·924
5	=	18·665	22·405
6	=	22·398	26·886
7	=	26·131	31·367
8	=	29·864	35·848
9	=	33·597	40·329
10	=	37·336	44·813

If it is desired to separate the phosphoric acid, the phosphates of alumina and iron may be treated with six times their weight of sodic sulphate, as before stated. Since, when operating in the usual way, the alumina is not recovered as alum, but as a salt of alumina, it is of importance to know whether alumina is contained in unadulterated flour, and if so in what quantity. It is certain that properly cleansed wheat contains no trace of alumina; but particles of clay from the ground, as well as sand from the millstones, do as a fact get into wheat flour, and there is no second-class flour in commerce which does not contain some small percentage of alumina. It might be expected that this adventitious alumina would have some sort of relationship to silica, for it may be presumed to exist as silicate of alumina. We fortunately

possess a few analyses by Dr. Dupré, and an elaborate research of Mr. Carter Bell, which will very fairly settle the question. Dr. Dupré analysed twelve commercial samples of flour, none of which gave any reaction with the logwood test, and the results of the quantities of alumina and silica are as follows :—

	Alumina, Per cent. of Ash.	Silica, Per cent of Ash.	Ratio.
Minimum, . . .	·63	3·08	1 : 4·7
Maximum, . . .	3·72	26·91	1 : 7·2
Mean, ...	1·98	10·4	1 : 5·2

Mr. Carter Bell analysed no less than forty samples of flour, none of which contained alumina as alum, and the following are the main results :—

	Alumina.	Silica.	Ratio.
Minimum, . . .	·003	·009	1 : 3·0
Maximum, . . .	·011	·109	1 : 9·1
Mean, ...	·004	·034	1 : 8·6

Mr. Carter Bell also analysed thirty-two samples of bread, none of which gave any reaction with the logwood test; the main results of these analyses are as follows :—

	Water.	Silica.	Iron Phosphate.	Alumina Phosphate.
Minimum, . . .	40·30	·010	·0005	·0022
Maximum, . . .	49·50	·039	·0040	·0082
Mean, . . .	45·56	·016	·0018	·0049

In these last researches with relation to bread, the ratio between the silica and alumina is 1 of silica to 7·1 of alumina. If the alumina is translated into alum, the important result is obtained that the number of grains of alumina, if calculated into alum, about equals the silica. Thus, in the mean of the thirty-two samples of flour, the alumina was 4 mgrms. Now 4 mgrms. ·004 of alumina is equal to ·035 of ammonia alum, and the silica is ·034. Or, again, if the mean numbers of the silica and alumina of the thirty-two samples of bread are taken, there is ·016 silica to ·019 of the phosphate of alumina turned into alum. This, if calculated on the 4 lb. loaf, would be a little over 5 grains of alum. Hence from these researches it is clear, that in cases in which the analyst finds the presence of alum in bread from tests detailed, and then burns a quantity of the bread up, and in the ash estimates the phosphate of alumina and the silica, it will be a perfectly fair calculation, *to allow for every part of silica found one part of alum, and this quantity is to be deducted as natural to the flour in the final calculation.*

BIBLIOGRAPHY RELATIVE TO FLOUR AND BREAD.

All the general treatises, without exception, enumerated at page 43 have articles or chapters on flour and bread, and may be consulted.

BALA.—Farine de blé adultérée par de la farine de Lathyrus. *Union Pharm.*, 1861, t. ii., p. 151.

BARRNEL.—Sur une prétendue falsification du pain par les sulfates de cuivre et de zinc. *Ann. d'Hyg. et de Méd Lég.*, 1832, t. vii., p. 198.

BELL, J. CARTER.—On Analysis of Flour and Bread. *Analyst*, vol. iv., 1879, p. 126.

BIBRA, V.—Die Getreidearten u. das Brod. Nürnberg. 1871.

BLYTH, A. WYNTER.—Note on "Alum in Bread," *Analyst*, June, 1878; Improved Processes for the Detection and Estimation of Alum in Bread and Flour, *Analyst*, Jan., 1882; Art. "Bread" in *Dictionary of Hygiène.* Lond. 1876.

BOLAS, THOMAS.—*Chem. News*, 1873; *Dingler's Polytechn. Journal.* Bd. 209, §. 399.

BRIOIS, C. A.—Sur le gluten et le mélange de différentes farines. (*Thèse de pharmacie.*) 1856.

CHEVALLIER.—Various papers on flour and bread adulteration. *Ann. d'Hyg. et de Méd. Lég.*, 1840, t. xxiv., p. 82; *ib.*, 1841, t. xxvj., p. 126; *ib.*, 1842, t. xxvij., p. 306; *ib.*, 1843, t. xxix., p. 39; *ib.*, 1853, t. xli., p. 198; t. xliii., p. 171; t. xlix., p. 402; t. l., p. 147. *Journal d'Hygiène*, May, 1878.

COMAILLE.—*Journ. Pharm.* (4), iv. 108; also *Chem. Centralbl.*, 1877, 585.

CHEZEAU.—Sur la fécule de pommes de terre mêlée aux farines. *Journ. Pharm. et Chim.*, 1829.

CLEAVOR, E. L.—A New Method for the Detection of Alum in Bread. *Pharm. Journ.* (3), April, 1874, t. iii., p. 857.

CROOKES.—The Detection of Alum in Bread. *Chem. News*, 1872, t. viij., p. 383.

DUPRÉ, A.—*Chem. News*, 1876. Preliminary note on the Detection of Alum in Flour, *Analyst*, No. 28, 1878.

———The Detection and Estimation of Alum in Wheat Flour, *ib.*, vol. iv., 1879, p. 126.

FRANCHINI, ANTOINE.—"Palmelle prodigieuse." Bologne, 1880.

GANEAU.—"Alterations et falsifications des farines." Lille, 1856.

GAULTIER DE CLAUBRY.—*Ann. d'Hyg. et de Méd. Lég.*, 1847, t. xxxviij., p. 151; *ib.*, 1843, t. xxiv., p. 347; *ib.*, *Bull. de l'Acad. de Méd.*, 1871, t. xxvj., p. 729.

HADON.—Recherche de l'alum dans le pain. *Journ. Chim. Méd.*, 3e série, 1878, p. 240.

KUHLMANN.—Considérations sur l'emploi du sulfate de cuivre et de diverses matières salines dans la fabrication du pain. *Ann. d'Hyg. et de Méd. Leg.*, 1831, t. v., p. 339.

MAYER, W.—*Ann. de Chem. u. Pharm.*, Bd. 101.

MEYER, G.—*Zeitschrift f. Biologie*, 1871, p. 1.

ORFILA.—Sulfate de cuivre dans le pain. *Arch. Gén. de Méd.*, Mars, 1872; *Ann. d'Hyg. et de Méd. Lég.*, 1829, t. i., p. 297.

PAYEN.—Altération du pain. *Comptes rendus de l'Académie des Sciences*, Juillet, 1848; *Journ. de Pharm.*, xvi., p. 279.

POGGIALE.—Sur une altération spéciale et extraordinaire du pain de munition. *Bull. de l'Acad. de Med.*, 1871, t. xxvj.

RITTHAUSEN, A.—*Journ. Pract. Chem.*, lxxxv. 193; lxxxvj. 257; lxxxviii.

141 ; xci. 296 ; xcix. 439 ; ciii. 65, 193, 233, 273. Die Eiweisskörper der Getreidearten. Bonn, 1872.
RIVOT.—Sur l'examen des farines et du pain. *Annales des Mines*, 5 Ser., 1856, t. x., p. 131.
RODRIGUEZ.—Sur le mélange de la farine de froment avec d'autres farines. *Ann. d'Hygiène et de Méd. Lég.*, 1831, t. vj., p. 199 ; *Ann. de Chem. et Phys.*, t. lv., p. 45.
WANKLYN, A.—Alum in Bread. *Proceedings Soc. of Analysts*, i., 1876.
YOUNG, W. C.—Estimation of Alum in Bread. *Analyst*, June, 1878.

CHILDREN'S FARINACEOUS FOODS.

§ 91. There are a great variety of farinaceous foods in commerce, most of them entirely unsuited to be the food of young

TABLE XII.—INFANTS' FARINACEOUS FOODS.

	Salts.	Fat.	Albuminoids.	Carbo-hydrates.	
I. Biscuit foods, made from baked wheat flour and condensed milk :—				Soluble in Cold Water.	Insoluble in Cold Water.
Nestles', ...	2·17	3·67	9·85	41·16	37·85
,, ...	1·85	4·75	10·96	76·08	
,, ...	1·70	...	9·50	78·72	
Gerber & Co., in Thun, . .	1·45	4·75	13·69	75·72	
Anglo-Swiss, ...	1·74	5·02	10·33	43·51	33·55
,, ...	1·46	5·44	8·84	48·5	27·95
Giffey, Scheele & Co., in Rohrbach, ...	1·78	4·34	12·86	47·68	29·94
Faust and Schunster in Gottingen,	1·76	5·83	10·71	48·62	27·59
,, ,,	1·85	4·75	10·96	39·12	34·70
II. Other varieties of condensed infants' foods :—					
Gerber's lacto-leguminose, . .	2 to 3 (0·4 to ·05 of SO_3)	5 to 6	18 to 20	70 to 65	
Liebig's children's soup, . .	1·71	0·82	8·41	48·61	
,, lacto-leguminose, . .	3·01	1·34	20·47	16·25	49·41
French's children's flour, . . (according to the German patent made of sugar mixed with wheat flour.)	2·00 (·69 PO_5)	4·26	16·80	71·09	
Ridge's food, ... (a mixture of various flours.)	1·13	1·95	9·65	8·12	75·47
Dr. Coffin's food, N.Y., . . (made chiefly from leguminose flours.)	3·02	1·59	17·15	35·12	34·82

infants. A child at the breast is more of a carnivorous than an omnivorous animal; and will digest all kinds of meat-broth, meat itself, and albuminous fluids with comparative ease; but if, instead of the natural milk of the mother, a large amount of starchy and saccharine food is given, so little may be digested that the infant is starved.

Some of the farinaceous foods, like, for example, "Polson's Patent Flour," consisting of the flour of Indian corn, are made entirely from one ingredient; the majority are, however, mixtures of starchy, saccharine, and albuminous powders.

A few examples of these foods are given in the preceding Table (XII.)

OATS, OATMEAL.

§ 92. Of the various species of oat the *Avena sativa* and *Avena orientalis* are the two chief species now cultivated; but the varieties of these two species, according to soil, method of cultivation, &c., are very great.

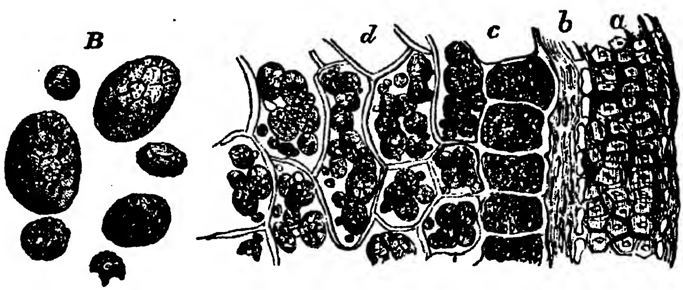

Fig. 21 is a section of the oat, × 190: *a* is the outer layer corresponding to the bran of wheat; *b*, the cells of the inner covering of the seed; *c*, the gluten cells; *d*, starch-holding cells. The starch granules at *B* are multiplied by 350.

As met with in commerce, oats consist of the seeds enclosed in their paleæ or husk. The mean composition of the ground oats, or oatmeal, is as follows:—

	Per cent.
Water,	12·92
Nitrogenous matter,	11·73
Fat,	6·04
Sugar,	2·22
Dextrine and gum,	2·04
Starch,	51·17
Fibre,	10·83
Ash,	3·05

The nitrogenous substance is composed of gliadin and plant-caseine. The "gliadin" (according to H. Ritthausen and U. Kreusler) has a much higher percentage of sulphur than the gliadin of wheat; the sulphur being 1·66 per cent. of the substance, while wheat gliadin has ·85 per cent. of sulphur. The plant-caseine has the composition of legumin, but the properties of gluten-caseine. Von Bibra also states that oatmeal has 1·24 to 1·52 per cent. of albumen. The oat possesses a greater proportion of fat than other cereals. The composition of the fat is as follows [*König*]:—

	Per cent.
Glycerine,	2·8
Oleic acid,	60·5
Stearic and palmitic acids,	36·7

Hence it follows that there is some free fatty acid.* The composition of the ash of oats is as follows:—

	Per cent.
Potash,	17·00
Soda,	2·24
Lime,	3·73
Magnesia,	7·06
Ferric oxide,	·67
Phosphoric acid,	23·03
Sulphuric acid,	1·36
Silica,	44·33
Chlorine,	·58

The richness of oats in oily matters and in protein compounds is an explanation of its great nutritive powers.

Adulteration.—The chief adulteration of oatmeal is with barley-meal, and more than one conviction has taken place in this country for quantities of from about 15 per cent. The method of detecting and estimating this adulteration is wholly by microscopical means, and is detailed at page 139. The defence which is to be expected in prosecutions for adulterated oatmeal is, that the barley has become mixed with the oats in an accidental manner. As a fact, genuine samples of oatmeal frequently contain some barley starch, so that it is only a question of quantity. Should, however, the barley starch show anything like 2 or 3 per cent., such percentages have not been yet known to occur save as wilful or fraudulent admixture in oatmeal, and the analyst should not have the slightest hesitation in certifying and letting the case be tried upon its merits.

* There is some free acid, if the amount of glycerine is correct; but the saponification was by lead oxide, which gives a lower percentage of glycerine than when potash is used.

BARLEY.

§ 93. There are several species of barley under cultivation in this country, all of which may, however, be considered as varieties of the following species of hordeum: — *H. hexastichon*, *H. vulgare*, *H. zeocriton*, and *H. distichon.* It is used as a food in the form of "barley-meal," the grain being ground whole, and as pearl barley, the latter being the grain deprived of its coverings and rounded by attrition. Barley-meal in the time of Charles I. almost entirely took the place of wheat as the food of the common people, especially in the north of England. The composition of barley-meal is as follows:—

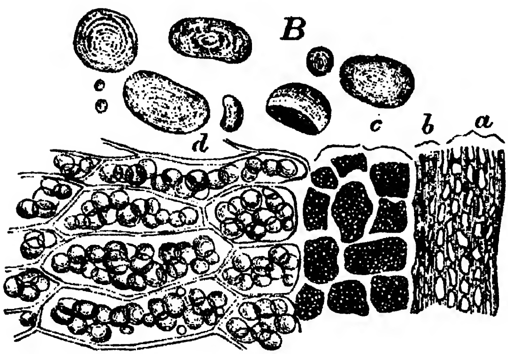

Fig. 22 is a section of barley, ×190: *a* is the layer of cells forming the outer coat of the seed; *b*, the inner; *c*, the gluten cells, and *d* the starch-holding cells. *B*, barley starch, ×350.

	Per cent.
Water,	15·06
Nitrogenous substances (albumen, 1·0 to 1·7 per cent.),	11·75
Fat,	1·71
Carbo-hydrates (sugar, 1·2; dextrine, 1·7),	70·90
Woody fibre,	·11
Ash,	·47

The nitrogenous substances are, it would appear, similar to those of wheat, comprising albumen, gliadin, gluten-caseine, gluten-fibrine, &c. The constituents of the ash of barley are as follows:—

	Per cent.
Potash,	20·15
Soda,	2·53
Lime,	2·60
Magnesia,	8·62
Ferric oxide,	·97
Phosphoric acid,	34·87
Sulphuric acid,	1·39
Silica,	27·64
Chlorine,	·93

Barley-meal is used as an adulterant of various foods, but in

itself it is little tampered with. The detection of adulterations is mainly microscopical, and the dimensions and appearances of barley-starch are described at page 142.

Barley Bread.—Barley bread, though but little used in England, is eaten in some parts of the Continent. The mean of two analyses by Von Bibra is as follows :—

	Per cent.
Water, ...	12·39
Nitrogenous substances, . . .	5·91
Fat,	·90
Sugar, . .	3·95
Carbo-hydrates,	71·03
Woody fibre,	5·63

RYE.

§ 94. The seed of the *Secale cereale*, in the form of rye-bread, was once a common article of diet in England, and it is now used as the daily bread of the northern European nations. The mean composition of rye flour is as follows :—

	Per cent.
Water, ...	14·24
Nitrogenous substances, . . .	10·97
Fatty matters, ...	1·95
Sugar, ...	3·88
Gum, ...	7·13
Starch, ...	58·73
Woody fibre, ...	1·62
Ash, ...	1·48

The nitrogenous substances in rye are made up of albumen, mucedin, and gluten-caseine, but gluten-fibrine and gliadin do not appear to be present. The fat extracted from the rye has, according to König, the following composition :—

	Per cent.
Glycerine, ...	1·30
Oleic acid, ...	91·60
Palmitic and stearic acids, . . .	8·10

It, therefore, consists only in part of glycerides, some of the acids being in the free state.* The gum, according to M. H. Ritthausen, is soluble in alcohol, and has the ordinary composition of gum.

* The fat was saponified by lead oxide. (See the note on page 175, and the observations in the article on "Olive Oil.")

The ash of the rye-flour has, according to V. Bibra, the following composition :—

	Per cent.
Potash,	38·44
Soda,	1·75
Lime,	1·02
Magnesia,	7·99
Ferric oxide,	2·54
Phosphoric acid,	48·26
Sulphuric acid,	...
Chlorine,	...

The composition of fresh rye-bread, according to twenty-seven analyses, from various sources, collected by König, is as follows :—

	Minimum. Per cent.	Maximum. Per cent.	Mean. Per cent.
Water,	35·49	48·57	44·02
Nitrogenous matters,	3·49	9·22	6·02
Fat,	0·10	·83	·48
Sugar,	1·23	4·55	2·54
Carbo-hydrates,	32·82	51·13	45·33
Fibre,	·29	·39	·30
Ash,	·86	3·08	1·31

None of the cereals are so liable to become ergotised as rye. [See vol. ii., article on "Ergot."] Roasted rye has been used to adulterate coffee, chicory, and other substances. It furnishes, by appropriate treatment, a good malt for the distillation of spirits, and is used in the manufacture of Hollands.

RICE.

§ 95. Rice is obtained from the *Oryza sativa*, and the term is popularly applied only to the seed denuded of husk and inner cuticle, the composition of which is as follows :—

	Per cent.
Water,	14·41
Nitrogenous substance,	6·94
Fat,	·51
Starch,	77·61
Woody fibre,	·08
Ash,	·45

The oil which is obtained from the rice embryo has a density of ·924 at 15°, and at 5° becomes thick and buttery; it contains much oleine and an albuminous substance.*

* A. Pavesi, and E. Rotondi, *Gazetta Chemica Italiana*, iv. 192-195.

The composition of the ash of rice is as follows :—

	Per cent.
Potash,	21·73
Soda,	5·50
Lime,	3·24
Magnesia,	11·20
Ferric oxide,	1·23
Phosphoric acid,	53·68
Sulphuric acid,	·62
Silica.	2·70
Chlorine,	·10

Rice is said to be adulterated from time to time with other starches, but it is in itself so cheap that it is more likely to be

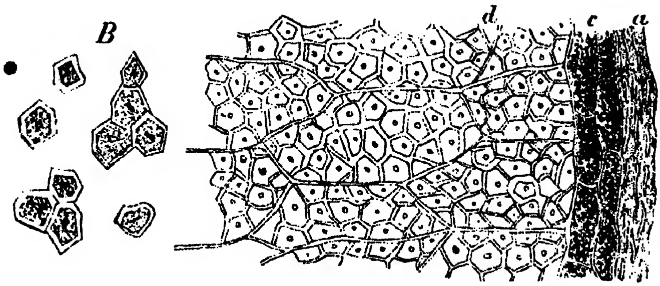

Fig. 23 represents the microscopical structure of rice. The figure is a section of the seed, × 190. *a*, is the outer husk, *c*, the gluten cells, and *d*, the starch-holding cells. B. The starch cells, × 350.

used as an adulterant than tampered with. The microscopical examination of a sample would easily detect any foreign matters. The size and characters of the little granules have been already described at page 143, and are entirely different from all the other starches. A chemical method of detecting the falsification of rice has been proposed by M. Van Bastelaer. It appears that a saturated solution of picric acid does not cause the least precipitate in a cold watery extract of rice; but if maize starch, leguminous starches, or other matters be present, there is a more or less abundant precipitate. The quantities recommended are 20 grms. of the powdered rice steeped for an hour in 100 grms. of water, and then the infusion decanted; to this infusion the picric-acid test is applied.

MAIZE.

§ 96. Maize, or Indian Corn (*Zea Mays*), a native of tropical America, is extensively cultivated in America, Africa, Southern Europe, Germany, and other countries. It is ordinarily met with as the Indian-corn meal of the shops, and forms the basis of many "infants' foods;" its use appears to be on the increase. According to a recent analysis of A. Riche, maize has the following composition:—

	Per cent.
Water,	17·10
Starch,	59·00
Albumen,	12·80
Oil,	7·00
Dextrine and sugar,	1·50
Cellulose,	1·50
Ash,	1·10
	100·00

According to König, the fatty matter of the maize contains 6·46 per cent. of glycerine, 79·87 per cent. of oleic acid, and 16·14 per cent. of stearic and palmitic acid. The mean composition of the ash from nine analyses of maize is as follows:—

	Per cent.
Potash,	21·73
Soda,	5·50
Lime,	3·20
Magnesia,	11·20
Ferric oxide,	1·23
Phosphoric acid,	53·68
Sulphuric acid,	·62
Silica,	2·74
Chlorine,	·10
	100·00

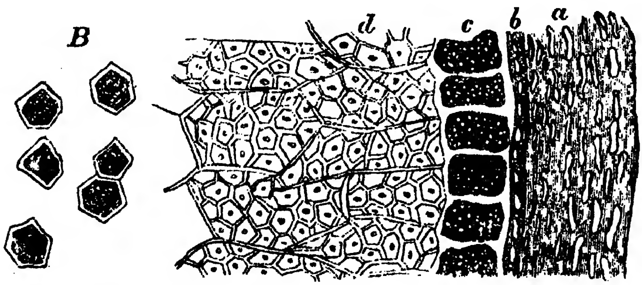

Fig. 24 represents a section of the seed, × 190; and B. the starch, × 350. *a* is the outer husk; *b*, the inner; *c* is the gluten cells; *d*, the starch-holding cells.

An aqueous decoction of maize gives with a little iodine a peculiar reddish-purple colour. On placing the iodised decoction in the dark, after some eight to twelve hours the precipitate becomes dirty white, and the supernatant fluid milky; if an excess of iodine is added the precipitate is then red, but it also becomes decolourised in the dark. Maize is said to be occasionally adulterated with potato starches, &c.; these a microscopical examination will at once detect. M. Genin has given certain chemical reactions, based upon the different hues which mixtures of maize and potato starch assume when treated with iodine, and also a process based on the volume which a precipitate obtained by lead acetate in an alkaline extract occupies in pure and adulterated samples. These processes are, however, far too loose to be of any service.

MILLET.

§ 97. The millet seeds are derived from two species of panicum, *Panicum miliaceum* and *Panicum italicum*. It is extensively used among the Chinese and Eastern races as an article of diet, and its nutritive power is about equal to that of rice.* The average composition of millet deprived of its coverings, according to six analyses, is as follows (König) :—

	Per cent.
Water,	11·26
Nitrogenous substance,	11·29
Fat,	3·56
Sugar,	1·18
Dextrine and gum,	6·06
Starch,	60·09
Cellulose,	4·25
Ash,	2·31

The composition of the ash of the millet deprived of husk is as follows :—

	Per cent.
Potash,	18·36
Soda,	3·82
Lime,	...
Magnesia,	21·44
Ferric oxide,	1·82
Phosphoric acid,	44·21
Sulphuric acid,	2·02
Silica,	8·33

* In the author's "Dictionary of Hygiène" will be found a remarkable experiment on the nutritive qualities of millet.

POTATO.

§ 98. The chemical composition of the uncooked potato is, according to the analysis of some fair average tubers, as follows:—

	Per cent.
Water,	76·00
Starch,	19·68
Sugar,	1·20
Albumen,	·70
Gum,	·40
Asparagin,	·30
Fat,	·30
Solanin,	·05
Nitrogenous substance,	·15
Insoluble matter,	·40
Ash,	·82
	100·00

A summary of seventy analyses, determining the principal constituents of the potato, is given by König as follows:—

	Minimum.	Maximum.	Mean.
Water,	68·29	32·22	75·77
Nitrogenous substances,	·51	3·60	1·79
Fatty matters,	·05	·80	·16
Starch,	12·05	26·57	20·56
Woody fibre,	·27	1·40	·75
Ash,	·42	1·46	·97

It is thus seen that, according to all analyses, some 95 per cent. of the potato is water and starch. The nitrogen of the potato, which, according to the old method of analysis, would be reckoned into albumen, or, at all events, into protein substance, is derived from albumen, asparagin, solanin, and amido acids. It has been calculated that about 56 per cent. of the total nitrogen is derived from asparagin and amido acids—a fact which must be remembered in diet calculations.

Besides the constituents enumerated, there are certain organic acids in the potato which may be extracted in small quantities by sulphuric acid and ether. Among these are citric and succinic acids, and possibly the presence of these organic acids in part accounts for the antiscorbutic power possessed by the potato.

The composition of the ash of the potato, according to fifty-three analyses by E. Wolff, is as follows:—

	Minimum.	Maximum.	Mean.
Potash,	43·95	73·61	60·37
Soda,	...	16·93	2·62
Lime,	·51	6·23	2·57
Magnesia,	1·32	13·58	4·69
Ferric oxide,	·04	7·18	1·18

	Minimum.	Maximum.	Mean.
Phosphoric acid, ...	8·39	27·14	17·33
Sulphuric acid, ...	·44	14·89	6·49
Silica, ...	...	8·11	2·13
Chlorine, ...	·85	10·75	3·11
Percentage of ash in dried substance, . . .	2·20	5·30	3·77

The potato is very subject to a fungus disease, the life-history of which has of late years been very fully elucidated by various observers, and more especially by Worthington G. Smith. The fungus is named botanically *Peronospora infestans*, and the manner in which it grows, and its method of reproduction, is shown in the annexed woodcut (fig. 25).

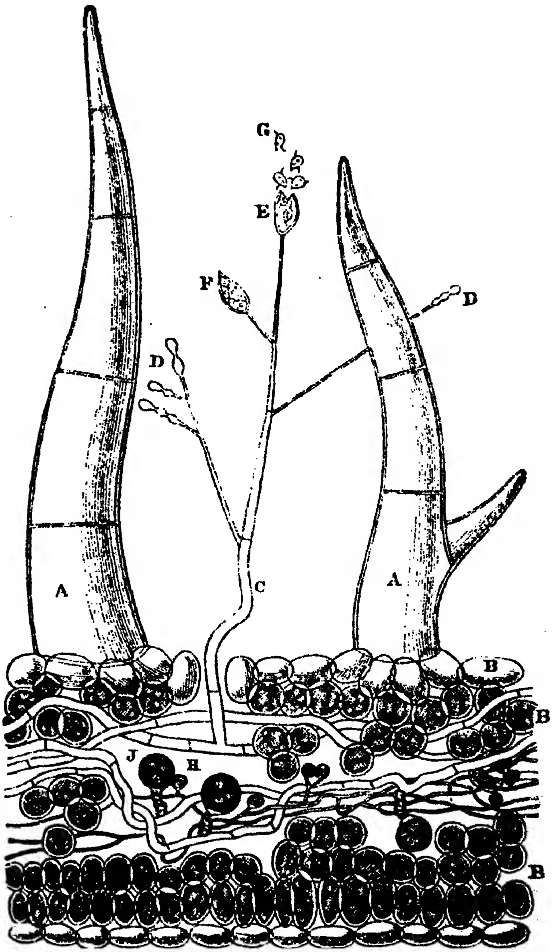

Fig. 25.

The figure represents the very highly magnified section of a potato leaf, and the mycelium of the peronospora growing among the cells. A, A are the natural hairs of the potato leaf; B, B are the upper and lower layers of the healthy cells. The threads and bodies at C, D, E, F, and G belong entirely to the fungus. The fine thread at C is a direct continuation of the spawn or mycelium living inside, and at the

expense of the leaf tissue. Emerging into the air, the thread is seen to bear two distinct species of fruit—one, D D, called simple spores or gonidia, while at E F are what are known as "swarm spores." The swarm spores, when moistened, set free fifteen or sixteen bodies, known as "zoo-spores," so named because they are endowed with spermatozoa-like motion, being furnished with two lash-like tails, which they move with great rapidity. A zoo-spore, when it falls on a leaf, has a surprising power of corroding the epidermis, and entering into the tissue. This action is probably due to some special solvent secreted by the zoo-spore. When movement ceases, the tails disappear, and a minute thread is protruded at one end, which develops into a network of mycelium. Both of these methods of production are asexual; but there is a third method which is sexual, and the more important, because, in this case, there are structures formed which resist frost and a variety of influences destructive of the former fragile structures. This third method is the production of oospores by the conjunction of two organs—the one named *antheridium*, and analogous to the anther of a flower, and the other *oogonium*, and analogous to the ovary of a flower. The oospores are dark-brown in colour, reticulated, and covered with little warty prominences about ·001 inch in diameter.*

Analysis of the Potato.—Since the potato is mainly composed of water and starch, a careful determination of those substances by the processes aleady enumerated will be sufficient for most purposes. For those in which great accuracy is not required, it will be sufficient to take the specific gravity of the potato, and then refer to the following table. This table, for fairly good

* The Peruvians make a national dish from frozen potatoes, which they call "chuno." The potatoes are steeped for a little while in water, then exposed for a few days to sharp frost, washed, and rubbed. By this method the peel becomes detached, and the starchy matters are dried in the sun or in an oven. The dried hard tubers are cut in thin slices and baked, and eaten with the addition of Spanish pepper. An analysis by Meisel (*Wagner's Jahresbericht der Chemisch Technol,* 1881) is as follows:—

	Per cent.	
Water,	13·030	
Starch,	81·844	
Nitrogenous matter,	2·313	Total nitrogen, ·4 %. Nitrogen soluble in water, ·03 %.
Woody fibre,	1·133	
Fat,	·182	
Ash,	·356	
Soluble constituents in water,	1·142	·400 sugar. ·141 asparagin. ·601 soluble starch, dextrine, soluble ash constituents, &c.

potatoes, will give results of from within ·3 to ·5 per cent. of the true value; but with regard to tubers poor in starch there may be a much larger error.

TABLE XIII.—SHOWING THE PERCENTAGE OF STARCH AND DRY SUBSTANCE CORRESPONDING TO VARIOUS SPECIFIC GRAVITIES.

Specific gravity.	Dry substance.	Starch.	Specific gravity.	Dry substance.	Starch.
1·080	19·7	13·9	1·120	28·3	22·5
1·081	19·9	14·1	1·121	28·5	22·7
1·082	20·1	14·3	1·122	28·7	22·9
1·083	20·3	14·5	1·123	28·9	23·1
1·084	20·5	14·7	1·124	29·1	23·3
1·085	20·7	14·9	1·125	29·3	23·5
1·086	20·9	15·1	1·126	29·5	23·7
1·087	21·2	15·4	1·127	29·8	24·0
1·088	21·4	15·6	1·128	30·0	24·2
1·089	21·6	15·8	1·129	30·2	24·4
1·090	21·8	16·0	1·130	30·4	24·6
1·091	22·0	16·2	1·131	30·6	24·8
1·092	22·2	16·4	1·132	30·8	25·0
1·093	22·4	16·6	1·133	31·0	25·2
1·094	22·7	16·9	1·134	31·3	25·5
1·095	22·9	17·1	1·135	31·5	25·7
1·096	23·1	17·3	1·136	31·7	25·9
1·097	23·3	17·5	1·137	31·9	26·1
1·098	23·5	17·7	1·138	32·1	26·3
1·099	23·7	17·9	1·139	32·3	26·5
1·100	24·0	18·2	1·140	32·5	26·7
1·101	24·2	18·4	1·141	32·7	27·0
1·102	24·4	18·6	1·142	33·0	27·2
1·103	24·6	18·8	1·143	33·2	27·4
1·104	24·8	19·0	1·144	33·4	27·6
1·105	25·0	19·2	1·145	33·6	27·8
1·106	25·2	19·4	1·146	33·8	28·0
1·107	25·5	19·7	1·147	34·1	28·3
1·108	25·7	19·9	1·148	34·3	28·5
1·109	25·9	20·1	1·149	34·5	28·7
1·110	26·1	20·3	1·150	34·7	28·9
1·111	26·3	20·5	1·151	34·9	29·1
1·112	26·5	20·7	1·152	35·1	29·3
1·113	26·7	20·9	1·153	35·4	29·6
1·114	26·9	21·1	1·154	35·6	29·8
1·115	27·2	21·4	1·155	35·8	30·0
1·116	27·4	21·6	1·156	36·0	30·2
1·117	27·6	21·8	1·157	36·2	30·4
1·118	27·8	22·0	1·158	36·4	30·6
1·119	38·0	22·2	1·159	36·6	30·8

PEAS.

§ 99. The pea is, without doubt, the most important of all the leguminous plants. The garden pea is derived from the *Pisum sativum*, a native of the south of Europe, but long naturalised in this country. The field pea, grown for the purpose of feeding cattle, is the *Pisum arvense.*

Forty-one analyses collected by König give the following values:—

	Maximum.	Minimum.	Mean.
Water,	22·12	11·01	14·31
Nitrogenous substance,	27·14	18·56	22·63
Fat,	3·30	·64	1·72
Nitrogenous free extractive matter,	59·38	41·90	53·24
Woody fibre,	10·00	2·22	5·45
Ash,	3·49	1·76	2·65

The 53·24 per cent. of non-nitrogenous soluble matter is composed of 36·03 starch, 5·51 dextrine, and 11·70 other substances, among which is some sugar. Cholesterine is also found in peas, but there have been no researches as to its exact quantity. The most important principle of the pea is "legumin." Its amount varies in different species. Thus, H. Ritthausen found in the green field pea, 3·95 per cent.; in the yellow, 9·45, and in the grey, 7·30 per cent.; in the garden pea, 5·40 per cent.

In the young unripe condition, peas contain much more water than the proportions given above. Thus, Grouven found in young unripe peas and beans the following:—

	Green Peas.	Green Beans.
Water,	79·74	91·34
Carbo-hydrates,	13·03	5·99
Albuminoids,	6·06	2·04
Salts,	1·12	·63

The albumen of peas (which may be obtained by boiling the solution after it has been freed from legumin) differs from ordinary vegetable albumen, both in elementary composition and in its behaviour to reagents. An analysis gives the following percentages:—

C, 52·94; H, 7·13; N, 17·14; S, 1·04.

After coagulation it dissolves in potash water to a clear liquid, which is not the case with vegetable albumen.

The analysis of the ash of peas gives the following as the extremes and mean of twenty-nine analyses:—

	Minimum.	Maximum.	Mean.
Potash,	35·80	51·41	42·79
Soda,	...	3·57	·96
Lime,	2·21	7·90	4·99
Magnesia,	5·80	13·02	7·96
Ferric oxide,	...	3·83	·86
Phosphoric acid,	29·30	44·41	36·43
Sulphuric acid,	...	9·46	3·61
Silica,	...	3·02	·86
Chlorine,	...	6·50	1·54

Peas, when putrid, undergo some peculiar change not yet investigated, resulting in the formation of a poison, perhaps similar to the cadaveric poisons described in the second part of this work.*

For the general analysis of peas, the water, the ash, and the amount of starchy matters are estimated by the processes already detailed. To separate the legumin, the peas must be powdered, or, if fresh, mashed into a paste, and treated with successive quantities of cold water, which may be advantageously feebly alkaline, but must not have the least trace of acid. The legumin may now be precipitated by acetic acid, the precipitate dissolved in weak potash, again precipitated, and then dried and weighed.

* Not very long ago a case of wholesale poisoning from this cause occurred in Salford. Many persons who had partaken of slightly decomposed peas exhibited symptoms of irritant poisoning. The peas were chemically examined, but contained neither arsenic, copper, lead, or other metallic poison. [*Phar. Journ.* (3), 294.] The subject of the formation of new and poisonous substances in such an article of food would well repay investigation. In Germany there has been used a condensed food made up of powdered and dried meat, incorporated with pea-meal, by strong pressure; it is scarcely necessary to say, that in this manner a food invaluable for the soldier is obtained, and one that contains in a very small compass all the essentials of nourishment. An analysis of these pea-meat tablets is as follows:—

	Per cent.
Water,	12·09
Nitrogenous matters,	31·18
Fat,	3·08
Carbo-hydrates,	47·50
Ash,	6·15

A condensed pea soup is also prepared. Two analyses of this condensed soup, given by König, are as follows:—

	1.	2.
Water,	7·58	8·08
Nitrogenous matters,	16·93	15·81
Fat,	8·98	24·41
Carbo-hydrates,	53·44	36·78
Woody fibre,	1·34	1·69
Ash,	11·73	13·23

Legumin is almost insoluble in cold or warm water; but since it may be extracted so easily from the fresh seeds, it is supposed to be in combination with phosphates of the alkalies when in its natural condition. But it is easily soluble in diluted alkaline liquids, and also readily dissolves in a solution of alkaline phosphates; if boiled it becomes insoluble in alkalies. Pure alkaline solution of legumin shows, with a little cupric sulphate, a beautiful violet colour. If impurities are present, such as gum or starch, the colour is blue. On boiling the alkaline solution, the legumin does not coagulate, but, as in the boiling of milk, a scum of altered legumin appears on the surface.

§ 100. *Preserved Peas.—Copper in Peas.*—Peas are preserved in several ways, sometimes by simply drying, when they form the well-known dried peas of the shops. But the more modern method is to heat the peas in a suitable tin capable of being hermetically sealed. The sealing is effected while the tin with its contents is at a high temperature. The rationale of the process is, that putrefying germs existing on the surface of the peas are destroyed, and fresh putrefactive agencies are prevented from gaining access by the exclusion of air. Peas so preserved may, as proved by analysis, be quite as nutritious as fresh peas. Preserved peas have often undergone a preparatory treatment by boiling in copper vessels, the object of which is to impart a fine green colour. M. Guillemare and M. Lecourt have, however, now patented a process by which chlorophyll has been substituted for the objectionable coppering. The copper that has hitherto been found in tinned peas has amounted to about 2 grains to 2·6 grains in the pound tin, and the question arises whether the copper is injurious to health in this proportion or not. In the cases appended to this article it will be noticed that men of considerable scientific reputation have expressed strong opinions on the subject; nevertheless, the whole of the injurious action of coppered peas rests entirely on theory, and in no single instance (although the consumption of coppered peas has been very large) has any really definite case been brought forward of actual poisoning by peas coloured in this way. It is perfectly true that it is not necessary for symptoms to arise, in order to pronounce whether a particular substance would be likely to be injurious or not; for example, the question would be answered readily enough that cyanide of potash was poisonous if in a certain quantity, although people might have taken small doses of cyanide of potash for some time without any apparent injury. But here the case is different; for it is by no means certain in *what particular combination* the copper exists, for if the copper should exist in a state of combination with some organic matter—for example, the legumin, so as to be insoluble

in the digestive juices, although the fact of such insoluble compound would render the peas less nutritious, yet they would have no toxic action. Legrif has found in the intestine of a healthy man ·036 to ·040 grm. of copper;* and Messrs. Paul and Kingzett have shown that, even when a soluble compound, like sulphate of copper, is ingested, most of it is excreted by the fæces.

The author, therefore, concludes that it would be best, in our present state of knowledge, to decline to state whether copper, when it exists in the moderate proportions given above,† would be likely to injure health, since there are no definite facts upon which to base a sufficient opinion. On the other hand, since coppered peas must either, (1.) have a toxic action, if the copper is in a soluble form, or, (2.) if the copper is insoluble, the pea must be deprived of some of its nutritious properties, the analyst need have no hesitation in certifying that peas made green with copper are adulterated under the Sale of Food and Drugs Act.

The method of detecting copper in peas is as follows:—A weighed quantity of the peas is made into a paste with water and a little hydric chloride, and the paste is placed in a proper platinum dish; a rod of zinc, on being inserted in the paste, so as to touch the platinum dish, sets up a galvanic current, and at the end of several hours all the copper is deposited as a coherent film, and may be dried and weighed. A neater process is the connection of the platinum dish with the negative pole of a battery, while the positive pole is suspended in the acid paste. In both instances the copper is deposited as copper.

Tinned peas may contain traces of tin. The process for the detection of tin is as follows:—A sufficient quantity of the peas is incinerated in a platinum dish, the ash is heated with strong hydric chloride, and evaporated nearly to dryness; a little water is then added, boiled, and the solution filtered. This method of extraction is repeated once or twice. The solution is now saturated with hydric sulphide, and any yellow precipitate filtered off. This should present the characters of sulphide of tin. Tin has been found, according to Mr. Hehner,‡ generally in tinned goods to the amount of 10 mgrms. in the English pound, and it has been supposed, without adequate proof, to exist as a stannous hydrate, a tin compound which is poisonous.

No prosecution has hitherto taken place with regard to tin in preserved goods; and in such small quantities as have hitherto been found, it is very questionable—presuming the tin to exist as stannous hydrate—whether any injury would result.

A few of the more important prosecutions for coppered peas may, in conclusion, be quoted:—

* Sonnenschein. † *Analyst*, 1877, p. 98. ‡ *Analyst*, 1880, 218.

In one of several similar cases heard at the Marlborough Street Police Court, it was proved by Mr. Piesse, the analyst, that the pound tin contained ·088 of copper, equal to 2¼ grains of sulphate of copper.

Dr. Conway Evans, Medical Officer of Health, stated his opinion, that the larger quantity of copper spoken of in a pound of peas, if eaten daily or repeatedly, would be injurious to health, and would produce chronic poisoning; but many persons might eat a quantity of these peas several times without apparently suffering any injurious effects, the period varying in accordance with difference of vigour, age, health, &c. Two or three doses might affect some persons and not others. From 14 to 15 grains of copper were sometimes given as an emetic; and sometimes, in ague or chronic diarrhœa, ⅛ to 3 grains were given as a tonic. It was a well-known medical fact, that in regard to some poisons (such, for instance, as mercury) certain persons were peculiarly susceptible to their influence; and it was possible that these peas containing copper, if swallowed by persons ignorant of their own susceptibilities, might (even in a single dose, or a few doses) lead to injurious consequences. He believed copper to be more fatal, in a smaller dose, than salts of lead. The heightening of the colours of preserves with copper was once a common practice. Cases of poisoning by copper were formerly very common, but copper utensils in cooking having given place to tin and iron saucepans, such cases were of rare occurrence. Pure metallic copper he believed to be harmless, but it was dangerous when in contact with other substances, and when dissolved.

Dr. Guy, F.R.S., said that cases of poisoning by copper had occurred in which the quantity swallowed must have been small. He had studied the question of poisons particularly; the fact of a trace of copper in the human body would not prove its existence in a poisonous form. He had made inquiries for Government into the effects of poisoning in certain trades; palsy followed the poisoning by copper. Two cases had come under his knowledge of poisoning by the green wall-paper in a room; the poisoning in his opinion came from the copper, not the arsenic. Salts of copper he considered more poisonous than lead; the small quantity of copper contained in the peas in question from France might prove injurious, and slowly undermine health. On a nervous person copper was more likely to produce dangerous symptoms than on any one else. With regard to the presence of 3·6 of copper, if taken one-third at a time, it would not affect a healthy person; but if repeated in small doses it would, in his opinion, be ultimately injurious to health. He considered that any article containing the amount of copper stated by Mr. Piesse should not be allowed to be sold for one moment. Sulphate of copper in its virulence ranked fourth in the class of poisons.

Dr. C. Tidy gave similar evidence. If copper, that is, sulphate of copper, were constantly taken to the extent of the amount of copper found in the French peas, it would be injurious to health.

Dr. A. Dupré stated that the quantity found was far beyond the quantity normally present in any vegetable.

Dr. Guy said he considered the sale of an article containing such a quantity of copper as that found in the French peas ought not to be tolerated. Small doses of copper were more dangerous than large ones, as the latter would cause vomiting.

A previous conviction against the defendant for the same offence was proved, but the prosecution stated that they desired publicity, not punishment, and a small fine was inflicted.*

* *Analyst*, 1877.

At the Liverpool Police Court a firm was prosecuted for selling peas containing copper equal to 2¼ grains of sulphate to the pound tin. A warranty produced.*

A Liverpool grocer was fined 20s. and costs, for selling peas containing copper equal to 2·6 grains of the sulphate to the pound.†

At Bradford vendors have been fined for selling coppered peas, the metal equalling 1¼ to 2 grains to the pound.‡

CHINESE PEAS.

§ 101. A pea or bean, much used in China in the form of cheese, is the *Soia hispida.*§ Its composition, according to G. H. Pellet, is as follows :—

	1.	2.	3.
Water,	9·000	10·160	9·740
Nitrogenous matters (coagulable nitrogen, 6·25),	35·500	27·750	31·750
Starch, dextrine, and sugar,	3·210	3·210	3·210
Cellulose,	11·650	11·650	11·650
Ammonia,	·290	·274	·304
Sulphuric acid,	·065	·234	·141
Phosphoric acid,	1·415	1·554	1·631
Chlorine,	·036	·035	·037
Potash,	2·137	2·204	2·317
Lime,	·432	·316	·230
Magnesia,	·397	·315	·435
Substances insoluble in acids,	·052	·055	·061
Not estimated mineral substances,	·077	·104	·247
Different organic matters,	15·289	25·539	24·127

* *Sanitary Record*, vi. 335. † *Ibid.*, vi. 351. ‡ *Ibid.*, vii. 63.

§ The pea-cheese is considered, in China and Japan, a very important food. The peas (*Soia hispida*) are soaked in water for about 24 hours, then strained; they are next ground to a thin paste with some of the water which has been put on one side. The grinding is effected by a mill. The matters are filtered, and the filtrate is concentrated by heat; and after skimming once or twice is cooled, the caseine coagulated by plaster, and a salt, which appears to be chloride of magnesium, added. The cheese is grayish-white, and has the following general composition :—

	Per cent.
Water,	90·37
Fatty matters,	2·36
Nitrogen,	·78
Ash,	·76

—M. Stanislaus Julien et M. Paul Champion, "*Industries de l'Empire Chinois.*"

LENTILS.

§ 102. The lentil is the seed of the *Erbum lens*, one of the Leguminosæ. Lentils are grown and eaten in all parts of the civilised world, and are highly nutritious. They contain, according to H. Ritthausen, 5·9 per cent. of legumin, and their general composition is as follows:—

	Per cent.
Water,	12·51
Nitrogenous substances,	24·81
Fat,	1·85
Carbo-hydrates,	54·78
Woody fibre,	3·58
Ash,	2·47

The general composition of the ash is as follows:—

	Per cent.
Potash,	34·76
Soda,	13·50
Lime,	6·34
Magnesia,	2·47
Ferric oxide,	2·00
Phosphoric acid,	36·30
Chlorine,	4·63

BEANS.

§ 103. The beans eaten in this country are mostly the kidney bean, *Phaseolus vulgare*, and the broad bean, *Vicia faba*. The following is the average composition of these vegetables:—

	Broad bean.	Kidney bean.
Water,	14·34	13·60
Nitrogenous substances,	23·66	23·12
Fat,	1·63	2·28
Carbo-hydrates,	49·25	53·63
Woody fibre,	7·47	3·84
Ash,	3·15	3·53

The percentage composition of the ash of these different beans has the following composition:—

	Broad bean.	Kidney bean.
Potash,	42·49	44·01
Soda,	1·34	1·40
Lime,	4·73	6·38
Magnesia,	7·08	7·41
Ferric oxide,	·57	·32
Phosphoric acid,	38·74	35·00
Sulphuric acid,	2·53	4·05
Silica,	·73	·57
Chlorine,	1·57	·86

From both the broad and the kidney bean a small quantity of cholesterine can be separated. According to Ritthausen, the legumin of the kidney bean has a composition different from that of other legumins; for while the percentage of nitrogen in pea and millet legumin amounts to 16·77 per cent., that of kidney bean legumin has only 14·71 per cent.

PART IV.—MILK, CREAM, BUTTER, CHEESE.

MILK.

HISTORICAL INTRODUCTION.

§ 104. Before the birth of experimental philosophy, the origin rather than the composition of substances was the subject of inquiry, and of fanciful and more or less ingenious conjecture. Milk to the ancient, as well as to the modern world, was a fluid of great virtue. Aristotle affirmed, "*Lac est sanguis concoctus, non corruptus,*" which may be translated, *Milk is elaborated, not decomposed, blood*—an opinion identical with that held by nineteenth-century philosophers.

Averroes, Avicenna, and others, reasoning in part from the difficulty with which many females conceive while suckling, held that milk was altered menstrual blood. Avicenna, indeed, formularised this doctrine by declaring that the menstrual blood of the pregnant was divided into three parts—part going to nourish the fœtus, part ascending to the breasts, and the remainder being an excrementitious product. These opinions may be traced to writers of a much later, almost modern epoch. The ancients were acquainted with only three constituents of milk—viz., butter, with which they used to anoint their infants; caseine, which they precipitated with vinegar; and the whey from which the curd and butter had separated, and this, up to the early part of the sixteenth century, constituted the whole of what was known as the composition of milk. Placitus enumerates no more constituents than Avicenna, but devotes several pages to the then all-important question as to whether milk was hot, cold, or moist, and concludes that animal milk, as compared with that of human, is cold, human with that of animal, hot. Placitus* was an upholder of the menstrual theory. Panthaleon† similarly cites with approval the dictum that *milk is a fluid superfluity, twice concocted in the breasts,* and gravely discourses, as stated, whether it is hot

* Sexti Placiti Papyriensis: *De Natura et Usu Lactis,* MDXXXVIII. It would appear, according to this author, that the Germans in his time used the milk of all animals, for he enumerates the milk not only of cows, mares, and goats, but also of pigs.

† *Summa Lacticinorum,* 1528.

or cold.* He recognises three parts only in milk—viz., serum, butter, and curd. His treatise is mainly composed of references to the ancients, and the usual disputations as to whether milk is hot or cold. The first mention of a fourth constituent of milk occurs in a curious work by Bartoletus, published in 1619. Bartoletus† called it the "manna" of milk, or "*nitrum seri lactis*." In his days sulphur, mercury, and a saline principle, were considered as the three active essences of all things, and as existing in all things; hence, Bartoletus, from the yellow colour of butter referred it to a sulphur principle, the whey, doubtless from its mobility, to quicksilver, and the curd to a saline element. He then compares milk with blood, also composed of a sulphurated, saline, and mercurial principle.‡ The discovery of Bartoletus for a long time was not known beyond Italy. A French apothecary, named Bartholomew Martin, writing in 1706,§ enumerates the constituents of milk as three—butter, analogous to sulphur, serum to mercury, and cheese to salt; but was not acquainted with milk-sugar, although eight years before Ludovico Testi‖ had written an entire treatise on it, calling it by the name it now bears.

In the early part of the eighteenth century, Leeuwenhoek discovered the microscopical characters of milk. He saw that it was a fluid containing many globules. Some, which he judged to be of a buttery nature, rose to the top of the liquid; and others, again, rather sank to the bottom, and were evidently different in composition.¶ Some twenty years later, A. Donné, in his *Cours Microscopique*,** published some beautiful plates of several kinds of milk, fresh and sour, human and animal, exhibiting the globules, &c., drawn to scale with wonderful accuracy.

§ 105. In the early part of the eighteenth century flourished the school of the illustrious master Boerhave, who laid the

* There are several other treatises on milk about this epoch, but they nearly all, as, for example, that of Gesner (*Libellus de Lacte et Operibus Lactarius*, auth. Conrado Gesnero, Medico), consist of commentaries on the opinions of older writers, and are of no value.

† Bartoletus was an Italian physician, a professor at Bologna and Mantua, B. 1586, D. 1630. His work is entitled, *Encyclopædia Hermetico-Dogmatica sive Orbis Doctrinarum, Physiologicæ, Semioticæ, et Therapeuticæ*. Bononia, 1619, 4to. The quarto is little over 300 pages, and is divided into five parts, viz., (1.) Physiology, (2.) Hygiène, (3.) Pathology, (4.) Semiotics, and (5.) Therapeutics.

‡ "*Enim in lacte videre est, in quo serosa portio mercuriali liquori, butyrosa sulphureæ, caseosa vero saline substantiæ respondet. Ita in sanguine alia sulphureæ, alia saline, alia mercurialæ substantiæ proportionaliter respondet.*"

§ *Traité du Lait*, par Barth. Martin, Apothicaire, Paris, 1706.

‖ *Relazione concernente il Zucchero di Latte*, 1698.

¶ *Letters*, tome ii., 4to edition, 1722.

** *Cours de Microscopie*, 8vo. Paris, 1844; *Atlas*, in folio. Paris, 1845.

foundations of animal chemistry. Boerhave saw in milk the most perfect food, and to him it was a fluid containing, wrapt up in mystery, all the elements of the body. Hence he laid the greatest stress on the importance of its study, and without doubt his example and teaching were the immediate cause of the numerous experiments carried out by his disciples, Vullyanoz, Doorschodt, and others. Boerhave says*—

"An animal is composed of matter which was not that animal before, but is changed into it by the vital power of the animal . . . . Milk, therefore, appears to be the first thing to be examined, for this is a true chyle, and much less diluted with the lymph than the chyle when poured into the subclavian vein, and therefore approaches nearer to the aliment. It has flowed through the veins, the heart, the lungs, and the arteries, and therefore has been mixed with all the juices, and being afterwards separated by the particular structure of the breasts, it may be collected and examined apart. Milk is a liquor prepared from the aliment chewed in the mouth, digested in the stomach, perfected by the force and juices of the intestines, and elaborated by means of the mesentery and its glands and juices, and the juices of the thoracic duct; it has undergone some actions of the veins, arteries, heart, lungs, and juices, and begun to be assimilated, yet may be had separate and discharged out of the body. And thus, by their own milk prepared from the proper matter of the chyle, all the known animals that have milk are nourished, both male and female; for milk is always prepared from the chyle as well in men as in women, as well in virgins and barren women as in mothers and nurses. Whence every such animal consists, is nourished, and lives on its own proper milk, and from this alone prepares all the other parts, both the solid and fluid, by means of the vital actions. It is now certain that men may live for years upon milk alone, and perform all the actions of life, and have all the solid and fluid parts of their bodies perfectly elaborated thereby. The serum, therefore, the blood, the lymph, the spirits, bones, cartilages, membranes, and vessels, proceed from milk, and if a man may live for years upon milk alone, milk must contain in itself the matter of all the parts of the human body."

Boerhave appears to have tested milk with a great variety of reagents, and found that it was curdled by all acids, whether nitric, acetic, hydrochloric, or sulphuric, or by acid vegetable juices. He also distilled milk, and found that it gave no spirit on distillation. "It also appears not to contain any trace of saline matter, being inodorous and perfectly insipid, and causing no pain if dropped into the eye." On boiling milk with alkalies, Boerhave was the first to notice the yellow colour caused by the decomposition of the sugar. He thought that a similar change took place in fevers, for he notices the yellow milk of feverish women, and warns the physician that he must not suppose the yellowness to be caused by an acid, but rather by an alkaline tendency, and by too much heat. Boerhave paid

* "The Practice of Chemistry," translated from Boerhave's *Elementa Chemicæ*. By Peter Shaw, M.D., 2nd ed. Lond. 1741, 2 vols., 4to.

particular attention to the state of the milk in fevers and infectious diseases; "and in the last contagion among the cows, whilst their meat remained in the stomach, and was neither discharged upwards by ruminating nor expelled downwards, and therefore truly putrefied with the violent degree of heat, so that the stomach was almost scorched with heat, as we explained the thing . . . Then the milk grew sharp, yellow, somewhat fœtid, and thin in the dug, and in this form was either milked out or dropped spontaneously." He also condemned the use of milk from heated or improperly fed animals, or those suffering from fever, and remarked that it would be found of a fœtid urinous odour, yellow in colour, thin, of a saline ungrateful taste, and acquiring, after a time, an odour of rancid cheese.*

§ 106. Boerhave, so far as is known, made no quantitative determination of any of the constituents of milk; but a very early attempt is found in a research undertaken by Geoffroy, published in 1737.† This experimenter took 12 lbs. of milk, and after coagulating the fluid, heated it gently over the fire, in order to separate the coagulum more completely. The liquid was now filtered, and the serum and coagulum both weighed. The serum weighed 8 lbs., the coagulum 2 lbs. 7 ozs. The serum was then evaporated to dryness, and left a residue weighing 7 ozs. 24 grains; in other words, it amounted to 5·2 per cent.; and since it must have been mainly composed of milk-sugar and salts, the determination is almost as exact as that of any analysis of the present day. He now appears to have distilled the residue, and obtained empyreumatic products, and a "*caput mortuum*,"‡ from which he extracted soluble salts by lixiviation, and among these salts he recognised chloride of sodium by its cubical crystals.

Doorschodt§ experimented on milk, possibly under the immediate superintendence of Boerhave; for he distilled it, and noticed that the distillate was neither acid nor alkaline, concluding, hence, that water alone was condensed, and that there was no other volatile principle. He also boiled the milk with alkalies, and details with great precision the successive changes of colour. He appears to have been the first to notice that alcohol coagulates

* A work by Dumonchaux, about the period of the Boerhave school, *De Lacte Mammarum et Pinguidine*, Petrus J. Dumonchaux, Duaci, 1754, contains nothing new about the composition of milk, but merely cites the opinions of others.

† *Commercium Literarium ad Re Medicæ et Scientiæ Naturalis Incrementum Institutium*, &c., 1737.

‡ The *caput mortuum* was the name of any residue left after distillation in the retort.

§ Henricus Doorschodt: *De Lacte*, 1737.

milk, and also that it may be preserved by borax and other antiseptics.

§ 107. M. Vullyanoz, another disciple of Boerhave, published a tract,* in 1756, on the essential salt of milk, which tended greatly to spread a knowledge of the substance discovered by Bartoletus, and described so fully by Testi the Italian. It would appear from his treatise that sugar of milk was then an article of commerce, but that there was great difficulty in preparing it white and pure. "There is in Switzerland a chemist named Creuzius who has composed the salt admirably, but unfortunately he will not impart his secret to any one. This is the more vexatious, because the salt he is proprietor of is infinitely finer than the others; it is whiter, sweeter, and dissolves better on the tongue." The method used in the time of Vullyanoz was simple evaporation, but he complains that the product was often "sour," and was not the same as the Swiss sugar. Vullyanoz established the fact that all herbivorous animals, as well as women, gave sugar of milk; he also investigated the solubility, and found it insoluble in hot alcohol, in spirits of ammonia, and in very pure aqua fortis, &c. Noticing that it effervesced with nitric acid, he made experiments which proved it to be a neutral salt, and thence drew an analogy between milk-sugar and soap, concluding that the latter contained an oil and also an acid, that it could be fermented, and that on distillation it yielded an acid, and was decomposed by sulphuric acid.†

§ 108. The next important paper on milk in order of time, is that of Voltelenus,‡ important because his experiments were quantitative. He took 42 ozs. of cows' milk and distilled it. The process was conducted very carefully, and occupied many days, and, as may be expected, was very troublesome, from the irregular bursts of ebullition. By the fifth day he obtained 29 ozs. of distillate "*Aqua Lactis Destillata;*" in other words, his determination of water was 69 per cent., much below the truth. The residue in the retort weighed 2 ozs. 3 drms., and effervesced with alkalies. He now increased the fire, and obtained an unctuous oil, weighing 14 drms., mixed with what he calls an oily

* "Sur le sel essentiel de Lait." Par M. Vullyanoz, Docteur en Médecine a Lauzaume. "Recueil Périodique, Observations de Médecine, Chirurgie, Pharmacie," &c. Par M. Vandermonde, 1756.

† Subsequent to the work of Vullyanoz appeared a treatise on milk-sugar, "Abhandlung vom Milch-Zucker," Braunschweig, 1772, by G. R. Lichenstein, who considered it an earthy salt, and called it *terra-oleosum sal mediam.*

‡ Floris Jacobi Voltilenii: *De Lacte Humano ejusque cum Asino et Ovillo Comparatione,* &c. Lipsiæ, 1779.

spirituous matter, acid, acrid, and like the spirit from guaiacum wood. The carbon in the retort weighed 10 drms., but on burning to an ash it weighed 3. The ash, boiled with water, left 2 drms. insoluble. In other words, he determined the ash to be ·89 per cent., and the soluble portion ·31 per cent. Hence, Voltelenus most certainly made a correct determination of the amount of saline matters in milk, and was probably the first who did so. Voltelenus next made a similar experiment with women's milk, taking 32 ozs., from which, in thirteen days, he had distilled over 31 ozs. 6 drms. of odourless liquid. Here, unfortunately, his retort broke; but he concluded that human milk is resolved by fire into much water and spirit; a double oil, a double salt, fixed and warm alkali and earth, to which may be added a "*spiritus sui generis.*" He refers to sugar of milk, and affirms that he has separated a similar substance from human milk. The same process was applied to asses' milk, 32 ozs. being distilled over a sand-bath in three days. On the first day a lactescent distillate came over, in quantity amounting to 1 oz. 17 drms. 1 scr.; on the second day, a more limpid liquid, amounting to 19 ozs. 4 drms.; and on the third day there came over 6 ozs. 1 drm. 1 scr., of a feebly acid liquid; by the fourth day he had to increase the heat, and obtained a black opaque oil, which separated on standing into three parts—a thick substance, a thinner, and what he calls a spirit. The carbon in the retort was weighed and then burnt. The ash weighed 3 drms., and on lixiviation the insoluble portion weighed 2 drms. 1 scr. He made precisely similar experiments on the milk of the sheep—identified salt, determined the amount of ash, &c. He thus came to the conclusion that all milk had the same constituents.

§ 109. Schoepff, in a very learned paper,* containing full references to the works of his predecessor, was the first who noticed the yellow colour of the whey—"liquidem colore diluti citrinum." He crystallised milk-sugar, and determined its amount with fair accuracy; but did not know exactly what it was, for the crystals were of a yellow colour, and reddened syrup of violets; hence, they were probably contaminated with lactic acid and colouring-matter.† One of the last workers on the chemistry of

* *Specimen Inaugurale Chemico-medicum de Variis Lactis Bubuli Salibus aliisque Substantius in ejusdem parte Aquosa Contentis*, &c. Ludovicus Augustus Schoepff, 1784.

† Previous to Schoepff, Beaumé appears to have made an accurate determination of the amount of salt in milk, saying that the third evaporation yielded crystals of sea salt, in the proportion of 7 to 8 grains per pint. Beaumé: *Dict. de Chimie*, ii., 1778, 498. Rouellium denied that the crystals were those of sea-salt, but considered them "salis febrifugi sylvii."

milk, prior to the nineteenth century, was Scheele, who discovered lactic acid, and established that phosphate of lime was always present in the caseine. He considered, in fact, that the caseine formed with the lime a true combination, the proportion between the two being from 1 to 1·5 per cent. of calcium phosphate to every 100 parts of dried caseine.* Experiments similar to those recorded were undertaken by Hoffman, who determined the total solids of cows' milk to be 13·5 per cent.; of asses, 9·5; goats about 10 per cent.; and of human, 9. He exhausted the total solids by water, and evaporated and weighed the soluble matter thus extracted, but no accurate result followed; and, indeed, it is very difficult to dissolve out milk-sugar and salts fully from the milk solids, unless they have been previously deprived of their fat. Caspar Neumann repeated and enlarged the experiments of Hoffman; he made out that cows' milk contained 14 per cent. of total solids, and he also distilled milk as well as butter. From 16 ozs. of fresh butter, distilled in a retort, at first over a sand-bath, and afterwards over an open fire, there arose 1 oz. of liquor of no remarkable smell or taste; 1 oz. and half a drm. of a reddish acidulous liquor, which smelt like burnt butter; 1 drm. of a brownish-yellow oil; 3 ozs. 3 drms. of a yellow oil; 1 oz. 6 drms. of a white, and 5½ drms. of a yellowish-brown oil—all of a thick butyraceous consistence, and a volatile smell like that of horse-radish; and 1 oz. 6 drms. of a thin empyreumatic oil, which smelt like the *Oleum philosophorum*, that is, old olive oil distilled over from bricks. There was not the least mark of any volatile alkali in the whole process. The *caput mortuum* weighed 3½ drms.†

THE COMPOSITION OF COWS' MILK.

§ 110. Up to the present time the milk of the mammalia alone has been fully analysed. This has been found to consist of water, a peculiar sugar, albuminous bodies, a small amount of saline matter, and an emulsified fat. The milk of every class of animals has not, however, yet been examined completely; and although it may be presumed, on physiological grounds, that all milks contain qualitatively identical or analogous ingredients to those

* *De Lacte ejusque Acida: Nova Acta Acad. Reg. Sued.* Anni 1780; *Opuscula Chemica.*, vol. ii., p. 101-118.

† "The Chemical Works of Caspar Newmann," abridged and methodised, by Wm. Lewis. Lond. 1773.

of the cow, yet this has been by no means proved. The only milk, indeed, the composition of which we may be said to know with some real completeness is that of the cow, and this may be considered first.*

Cows' milk consists of matters partly in solution, and partly in suspension; sugar of milk, caseine, galactine, lactochrome, saline matters, and a few minute quantities of several other substances are dissolved in water, whilst milk-fat is apparently emulsified, and a portion of the caseine is in the form of extremely fine granules, which can only be arrested by filtration through porous earthenware, or a similar filtering medium. When a very thin layer of healthy milk is examined by a microscope, the milk-fat alone is visible, and appears in the form of innumerable globules, the number of globules depending on its richness in fat. Thus M. E. Bouchut found in different samples of milk the following varying numbers:—

Globules in a cubic millimètre.	Specific gravity.	Fat per litre.
1102500	1022	24
1820000	1021	21
1925500	1030	26
2105000	1028	29
2205000	1032	37
2305000	1028	29
2205000	1032	37
2400000	1030	37
2407000	1033	34
2692000	1030	29
3700000	1030	34

It would hence appear that good milk contains from about two to three and a half millions of globules in every cubic millimètre. It has hitherto been taught that the globules are surrounded by a thin pellicle or membrane, and, as a proof of the existence of this membrane, the fact is usually cited that, if you shake up milk with ether, scarcely any of the fat dissolves unless a little acetic acid is first added, which is supposed to act by dissolving the hypothetical membrane; but it may be shown that the fat can be extracted from milk by shaking with ether, provided that the volume of ether to that of the milk be excessive. Further, the globules are coloured by aniline red,† and their behaviour with moderate quantities of ether may be ascribed to

* The chemistry of the milk-secreting glands has scarcely been investigated. Bert (*Gaz. hebdom.*, 1879, N. 12) states that the gland contains a peculiar body which easily splits up with the production of a sugar by boiling with dilute sulphuric acid, or even simply with water.

† De Sinely: *Archives de Physiologie*, 1874, 497; F. Soxhlet: *Land. Versuch.*

the acids destroying the emulsifying property of the milk. Nor can one understand, on the "membrane" theory, how—when milk in thin layers is dried at the ordinary temperature of the air, and under conditions which involve no destruction of the membrane, should this exist—to account for the fact that ether so readily dissolves the butter fat. Hoppe-Seyler* has indeed, by estimation of the proportion existing between the water and caseine in cream, considered that a caseine layer exists round the fat globules; yet this must be so thin as not to be capable of estimation by weight. From these various facts the existence of the membrane is more than doubtful.

§ 111. *Amphioteric Reaction of Milk.*—Milk when tested immediately after its removal from the cow, has a peculiar action on litmus and turmeric paper, turning litmus blue and turmeric brown,—the so-called "*Amphioteric Reaction.*" On this point alone, although of no great importance, there is a most voluminous literature.† The amphioteric reaction of milk is similar to that shown by a solution of magnesium-hydric phosphate to which a little acid has been added, and is probably due to the acid phosphate of the alkalies existing in milk. It must also not be lost sight of, that there is a continuous development of CO_2 in milk, which gas in solution is always present; and this being the case, its feeble acid reaction must have an influence on the total reaction derived from other substances. Milk ultimately becomes decidedly acid, and has a constant tendency to acidity.

§ 112. *Total Solids of Milk.*—The amount of solid matter in milk varies within considerable limits, and is much influenced by all circumstances that affect the health and nutrition of the cow, certain cows secreting double and treble the normal amount of fat. The remark just made refers to the entire residue *minus* the water; but if we subtract the water as well as the fat, then the percentage of solid matter varies but little, and in healthy, fairly-fed cows has never (save in some very rare and exceptional cases) been known to fall below 9 per cent. This very important fact, formerly much disputed, has been (or ought to have been) set at rest by the results obtained in the experiments of so many chemists, that it is scarcely worth while reviewing the evidence on which it is based. The numerous analyses of Wanklyn,

* *Archiv für path. Anatom.*, bd. xvij., s. 417, 1859.

† Those who wish to be very fully informed on this subject may consult "Kritisches u. Thatsächliches über die Reaction der frischen Milch," von J. Schlossberger, *Annal. der Chim. u. Pharm.*, b. 87, p. 317, 1852; *Idem.*, b. 96, p. 76. Also a paper by Vogel, *Journ. für Prakt. Chem.*, 1874, b. 8, p. 137, "Ueber das Verhalten der Milch zum Lackmus Farbstoffe."

Carter Bell, and others tend rather to show that the true lowest percentage of milk solids, *minus* fat and water, is a little above rather than below 9 per cent., and this fact is fully borne out by the original investigations conducted in my own laboratory. The highest amount of the same solids which the author has yet found in the secretion from healthy animals, reaches to about 11 per cent., so that at most there is an extreme fluctuation between 9 and 11 per cent.—a remarkable fact, which *à priori* would have been pronounced improbable, considering the complex nature of milk.

§ 113. *Milk-Fat.*—Pure dry milk-fat is at ordinary temperatures a solid fatty substance, with an agreeable taste, of specific gravity ·91200 to ·91400 at 37°·7 C. [100° Fahr.]; its melting point is 35°·8 C. Milk-fat, under the form of butter, is constantly tinted more or less yellow from dissolved lactochrome; but it may, by the use of suitable solvents, be obtained almost colourless.

According to Wigner, 1000 volumes of the pure fat expand from 37°·7 [100° Fahr.] to 1047·2 at 100° [212° Fahr.], its average expansion being ·0780 for every degree Centigrade. This is, however, not perfectly accurate for the degrees between 65°·5 [150° Fahr.] and 87°·7 [190° Fahr.], the expansion being slightly in excess of the average rate; but the abnormal deviation between these degrees does not appear to be peculiar to milk-fat.* 1 grm. of fat requires for saturation 227·3 mgrms. of potassium hydrate (KHO). This observation (originating with Dr. Koettstorfer†) has been utilised by the food-analyst in the distinguishing between butter and other fats.

§ 114. Milk-fat is essentially an intimate mixture of the glycerides of the fatty acids—palmitic, stearic, and oleic—not soluble in water, and also of the glycerides of certain soluble volatile fatty acids, of which butyric is the chief, and caproic, caprylic, and capric acids minor constituents.

Palmitin, or *Tripalmitin*, $C_3H_5(C_{13}H_{35}O)_3\ O_3$, is a white solid fat, but little soluble in cold, but readily soluble in hot alcohol or ether. A mixture of stearin and palmitin crystallises in little needle-like tufts, and was at one time considered a definite single fat, and called *margarine*. On saponifying palmitin by means of an alkali, and subsequent decomposition, it yields glycerine, and 95·28 per cent. of its weight of palmitic acid.

Palmitic Acid ($C_{16}H_{32}O_2$) has a melting point of about 62°. It may be obtained in quantity from palm oil, and also from

* On the Ratio of Expansion by Heat of Butter-fat, by G. W. Wigner, F.C.S., *Analyst*, No. 43, p. 183.

† New Method for the Examination of Butter for Foreign Fats, by Dr. Koettstorfer, *Analyst*, No. 39, 1879, p. 106.

the saponification of spermaceti. When purified by repeated crystallisation from alcohol, it is a tasteless white fat, crystallising in tufts of needles.

Stearin, or *Tristearin*, $C_3H_5(C_{18}H_{35}O_3)O_3$, is a white solid fat, melting at about 66°, and is a special constituent of fats with high melting points. On saponification and subsequent decomposition of the soap by a suitable acid, 95·73 per cent. of stearic acid may be obtained.

Stearic Acid, $C_{18}H_{36}O_2$.—This acid is to be found in nearly all animal fats as well as in a few vegetable fats. Stearic acid is an article of commerce, and made upon a large scale, especially in the manufacture of stearine candles. For this purpose, animal fats are saponified by hydrate of lime; the lime compound is subsequently decomposed by dilute sulphuric acid, and the mixture of oleic, palmitic, and stearic acids submitted to strong pressure; by this means, the oleic acid is separated, and a mixture of palmitic and stearic acids obtained, which in commerce is known as stearin. From this commercial stearin, stearic acid may be obtained by solution in alcohol and fractional precipitation by acetate of lead or barium, the stearate of lead or barium, as the case may be, separating before the palmitate. On decomposing the salt with sulphuric acid, and dissolving the acid in boiling alcohol, stearic acid crystallises, as the solution cools, in white glistening needles or leaflets, which appear under the microscope as elongated lozenge plates. The melting point of stearic acid is 69°·4. If impure, it crystallises in needles. It is without odour or taste, does not feel greasy to the touch, and dissolves in all proportions in boiling alcohol or ether, from which it separates on cooling.

Olein, or *Triolein*, $C_3H_5(C_{18}H_{33}O_3)O_3$.—Over 40 per cent. of milk-fat consists of olein, which is a combination of oleic acid with glycerine, and is at all ordinary temperatures a fluid oil, solidifying about 5°, at first colourless, but soon becoming yellow from absorption of oxygen. It has the power of readily and copiously dissolving palmitin and stearin, and is readily soluble in absolute alcohol or ether. On decomposition, olein yields 95·70 per cent. of oleic acid, $C_{18}H_{34}O_2$.

Pure oleic acid is difficult to obtain, since it so readily oxidises. When perfectly pure, it is without colour, taste, or smell, and has all the appearance of a colourless oil; at a low temperature (4°), it crystallises in needles; on destructive distillation, among a variety of gaseous and liquid products, it yields an acid known as sebacic acid ($C_{10}H_{18}O_4$), which is a constant product when any oil containing oleic acid is destructively distilled. Oleic acid forms two classes of salts, normal and acid. The normal

oleates of the alkalies are soluble in water, but the other salts of oleic acid are insoluble in water, no exception being found even in the case of the acid salts of the alkalies. The oleates of lead and copper are soluble in ether, as well as in cold anhydrous alcohol. The analyst takes advantage of this fact, to separate the oleates of lead and copper from the stearates and palmitates, which are insoluble in ether.

Butyrin, *Caproin*, and *Caprylin* have not yet been separated in a pure state; they yield on saponification butyric, caproic, caprylic, and rutic acids respectively.

Butryic Acid, $C_4H_8O_2$.—There are two butyric acids, one, normal butyric acid, C_3H_7COOH, boiling point 163°·4, specific gravity ·9817 at 0° C.; the other, isobutyric acid, $C(CH_3)_2H.COOH$, boiling point 154°, specific gravity ·8598 at 0°. The latter has a less offensive odour than normal butyric acid. Butyric acid is found in several plants, such as the locust bean, the fruits of the *Sapindus saponaria*, in the *Tamarindus indica*, the *Anthemis mobilis*, the *Tancentum vulgare*, *Arnica montana*, the fruit of the *Gingko biloba*, and probably several other plants. Butyric acid is the characteristic fatty acid of butter, and butter fat contains nearly 7 per cent. of it. Butyric acid is volatile, and may be distilled unchanged; it is also soluble in all proportions in water, alcohol, and ether. Most of the salts are soluble: baric butyrate crystallises in long prisms with four atoms of water; zincic butyrate in anhydrous pearly tables, which are remarkably soluble; cupric butyrate is bluish-green, and but sparingly soluble. Calcic butyrate is a very characteristic salt, for it is more soluble in cold than in boiling water, consequently, when a solution is boiled some of the salt is precipitated. The most characteristic reaction of butyric acid is its easy etherification by treatment of sulphuric acid and alcohol. In this way is formed butyric ether, which has a powerful smell resembling that of pine-apples. Its specific gravity is ·902, and boiling point 119°.

Caproic Acid, $C_6H_{12}O_2$.—There are two caproic acids, the one, normal caproic acid, $C_5H_{11}COOH$, boiling point 205°; the other, isocaproic acid, $C_3(CH_3)_2H_5COOH$, boiling point 199° to 200°. Caproic acid occurs in a very large number of plants, and has been found in human perspiration and in cheese. It is almost insoluble in water, is volatile, and may be distilled unchanged. The caproate of silver is in large thin plates, almost insoluble in water, and but slightly sensitive to light. The caproate of barium is soluble.

Caprylic Acid, $C_8H_{16}O_2$—fusing point 58°, boiling point 236°. The amount of caprylic acid in butter is very small. It is slightly soluble in boiling water.

Rutic Acid, $C_{10}H_{20}O_2$.—A white crystalline solid, fusing about 29°·5. This acid, in combination with glycerine, also occurs in very minute quantity in milk-fat. It is even less soluble than caprylic acid.

§ 115. *The Albuminoids of Milk.*—The albuminoids of milk comprise at least three principles,—viz., caseine, albumen, and nuclein. To these a fourth substance used to be added—viz., lacto-protein; but this, as the author has shown,* is not a simple substance, and it is probable that it is a mixture of bodies approaching alkaloids in their composition. Caseine appears but little, if at all, different from alkali-albuminate, the minor differences which exist being, with probability, ascribed to impurities. It is true that when milk is filtered through a porous cell, caseine, for the most part, is left behind; while, if a solution of alkali-albuminate is similarly treated, it passes through. Experiment has, however, shown that a solution of alkali-albuminate shaken up with butter fat behaves exactly like caseine; and similarly, Soxhlet has proved that a concentrated solution of sodic carbonate precipitates both caseine and alkali-albuminate, provided they are under the same conditions, and that it does not (as asserted by Zahn) leave alkali-albuminate in solution.†

Hoppe-Seyler‡ does not adopt altogether this view; for although he states that without doubt no other albuminoid, in its properties, stands so near caseine as alkali-albuminate, yet the notable difference in its power of rotating a ray of polarised light, and its behaviour to rennet, separates caseine as a distinct substance. The caseine of either cows' or goats' milk, not only in acid fluids, but in perfectly neutral solutions, is coagulated by gastric juice or a watery extract of the stomach. This coagulation takes place slowly at common temperatures, rapidly on warming; and the cause of it, according to Hammersten, is a body distinct from pepsin. Hammersten finds that the caseine of cows' milk, in the absence of lime salts, is coagulated by the addition of an acid, but not by rennet. A solution of caseine which has been precipitated by an acid, run into lime water neutralised by very dilute phosphoric acid, quickly coagulates on the addition of rennet, but without rennet neither on the addition of an acid, nor on boiling. Hammersten considers that the chemical change produced in the coagulation of caseine by

* Composition of Cows' Milk in Health and Disease, *Jour. Chem. Soc.*, 1879.

† "Beiträge zur physiologischen Chimie der Milch," von Dr. F. Soxhlet. *Journal für praktische Chemie*, vol. 6, p. 1, 1872.

‡ Hoppe-Seyler, *Physiologische Chemie*, p. 930.

rennet, is the splitting up of the caseine into two bodies, one of which is precipitated, and an albuminoid, which remains in solution, and is neither precipitated by boiling, nor by any of the following reagents—acetic acid, potassic ferrocyanide, or nitric acid; but is precipitated by mercuric chloride, and also by Millon's reagent.

Caseine is precipitated by a variety of substances—lead acetate, cupric sulphate, alum, mercuric chloride, tannic acid, rennet, sulphate of magnesia, and mineral acids, if not too dilute; but none of these precipitate caseine in a pure state, the precipitate usually containing fat, nuclein, and phosphate of lime, the latter, as already stated (p. 200), in the proportion of from 1 to 1·5 per cent. of caseine. The best precipitant is sulphate of magnesia, which leaves the nuclein to a great extent in solution. The fat may then be extracted by ether; but the phosphate of lime is in true combination with the caseine, and only a portion of it can be removed. A solution of caseine in combination with sulphate of magnesia, and freed from fat, turns a ray of polarised light in weak alkaline solution, $-87°$; in very dilute alkaline solution, $-87°$; in strong alkaline solution, $-91°$. Pure caseine is a perfectly white, brittle, transparent substance, insoluble in water, but soluble in very dilute acid solution, as well as in very dilute alkaline solution; in each case there is little doubt that a true chemical combination is formed. The presence of phosphate of soda in a solution of caseine (as, for example, in the milk itself), prevents the precipitation by simple neutralisation by an acid, the caseine not falling down until the acidity of the liquid is decided. It has been shown by Schutzenberger that, on sealing up caseine in a tube and heating with baryta water, it behaves like albumen, and is resolved into the following substances:—The elements of urea (ammonia and carbon dioxide), traces of sulphurous acid, of sulphuretted hydrogen, of oxalic and acetic acids, tyrosine, $C_9H_{11}NO_3$, the amido-acids of the series $C_nH_{2n+1}NO_2$, corresponding to the fatty acids, $C_nH_{2n}O_2$, from amido-œnanthylic acid to amido-proponic acid—leucine, $C_6H_{13}NO_2$, butalanine, $C_5H_{11}NO_2$, and amido-butyric acid, $C_4H_9NO_2$, with a few less known or identified products. Many of these substances may be identified in putrid milk.

The amount of caseine in milk is fairly constant, being about 3·9 per cent.; and the author has never known it exceed 5 per cent.

Serum-albumen occurs in milk, in no respect differing from the albumen of the blood. By careful addition of an alkali, this albumen may be changed into alkali-albuminate—that is, into caseine; therefore, according to this view, the albumen in milk

may be considered the residue of an incomplete reaction. Albumen is not precipitated by acetic, carbonic, phosphoric, or tartaric acids. A small quantity of a dilute mineral acid does not precipitate; with a larger quantity of concentrated mineral acid the solution becomes troubled, and the deviation of a ray of polarised light increased; a still larger quantity of acid precipitates it as acid albumen. The best method to obtain a solution of pure albumen is to precipitate a solution by basic acetate of lead, pass carbon dioxide through the mixture, separate the carbonate of lead by filtration, and, lastly, pass through it hydric sulphide, to remove the trace of lead still existing. Albumen is then in solution, but with a little acetic acid, on evaporation, it may be obtained in the solid state contaminated slightly with acetic acid.*

Another method of obtaining albumen pure is by dialysis. The physical characters of solid albumen differ according to the method of separation. Albumen obtained by dialysis is in the form of a yellow transparent mass, specific gravity 1·314; but albumen separated in the ordinary way from milk, for the purpose of quantitative determination, is in yellowish flakes, brittle, without taste or smell, insoluble in water, alcohol, and ether, soluble in dilute caustic alkali, if gently warmed, and from this alkaline solution precipitable by an acid. The amount of albumen in milk is really fairly constant, and averages ·7 per cent. In healthy cows it is a very constant quantity, the chief deviation occurring directly after calving, when the amount may rise as high as 3 per cent., but this is always accompanied by a corresponding rise in the caseine. According to the author's experience, the albumen preserves a very constant relation to the caseine, the quantity of the latter being five times that of the albumen; so that if either the amount of caseine or albumen is known, the one may be calculated from the other with great accuracy.

Nuclein.—Nuclein is the organic phosphorus compound of milk, containing, according to Miescher, 9·6 per cent. of phosphorus. Its formula is $C_{29}H_{49}N_9P_5O_{22}$. It is by no means peculiar to milk, but has been found in the blood, in pus, in the yelk of eggs, in the liver cells, and in yeast cells. When freshly precipitated, it is a white amorphous body, somewhat soluble in water; freely soluble in ammonia, soda solution, and phosphate of soda. The special test distinguishing nuclein from other albuminoids is the presence of phosphorus, and the production

* Meggenhofen appears to have been one of the first who detected the presence of albumen in milk. He estimated the amount in cows' milk as ·59 per cent. *Dissertatio Inauguralis sistens indagationem Lactis Muliebris Chemicam.* C. Aug. Meggenhofen. Frankfort, 1826.

of no red colour, either by Millon's reagent, or by a copper salt: added to a solution of nuclein alkalised by soda lye, it forms a very definite compound with lead, the lead and phosphorus being in the proportion of Pb to P.

The method adopted by Hoppe-Seyler* to separate nuclein from pus, was isolation of the pus cells by Glauber's salts, washing with very dilute hydrochloric acid and much water; then extracting the nuclein by the aid of a very weak alkaline solution of caustic soda, and filtering (which in this case proves a troublesome operation), and precipitating by a mineral acid. The precipitate is again dissolved in weak alkaline solution, and again precipitated, and the process repeated until the nuclein is supposed to be in a fairly pure condition. Nuclein may be separated from milk on the same principles, first exhausting the solids by alcohol and ether to remove fat.

§ 116. *Milk-Sugar*, $C_{12}H_{22}O_{11}H_2O$.—Milk-sugar, so far as is known, is only found in human milk, the milk of the herbivora, and of the bitch. It is easily distinguished from other sugars; its specific gravity is 1·53; and its solution turns a ray of polarised light to the right 58°·2. It is soluble in six parts of cold, and 2·5 parts of boiling water; it is insoluble in absolute alcohol and in perfectly dry ether, but in dilute alcohol and commercial ether it is slightly soluble, the solubility in amount depending mainly on the percentage of water which the ether contains. At 150° it loses an atom of water without further decomposition; its watery solution is perfectly neutral, and has a sweet taste: the sweetening power of milk as compared with cane sugar is but feeble.

It reduces Fehling's copper solution in a proportion different from that of grape sugar (see p. 115). Milk-sugar undergoes lactic fermentation readily (see p. 217), but alcoholic with some difficulty. Milk-sugar is precipitated by acetate of lead and ammonia; neutral acetate of lead, even at a boiling temperature, neither precipitates nor changes it. The oxides of copper, of bismuth and silver are reduced by solutions of milk-sugar, and indigo is decolourised; these latter reactions are similar to those of grape sugar. When oxidised by nitric acid, milk-sugar yields mucic acid, acetic acid, and tartaric acids, and on further decomposition oxalic acid may be obtained.

By boiling milk-sugar for several hours with 4 parts of water and 2 per cent. sulphuric acid, neutralising with carbonate of lime, evaporating the filtrate to a syrup, a different sugar from lactose may be obtained in microscopical crystals. To this

* *Med. Chem. Untersuch.*, Hoppe-Seyler. Berlin, 4. Heft.

altered milk-sugar, the name of galactose has been given. Its action on polarised light is expressed as +83·22 at 15°; it is a fermentable sugar, and yields, on oxidation with nitric acid, twice as much mucic acid as milk-sugar.

The amount of milk-sugar in normal milk preserves a very constant relation to the percentage of caseine, being about ·1 grm. per every 100 cc. in excess of the caseine. Its average is about 4 per cent.

§ 117. *Mineral Constituents of Milk.*—The mineral constituents of milk have been fully and early investigated, and the following may be considered a very close approximation to their actual amount and character:—

Potassium oxide, K_2O,	18·82
Sodium oxide, Na_2O,	11·58
Calcium oxide, CaO,	22·97
Ferric oxide, Fe_2O_3,	·06
Chlorine, Cl,	16·23
Magnesium oxide, MgO,	3·31
Phosphoric pentoxide, P_2O_5,	27·03

Four analyses of milk ash by R. Weber and Haidlen the following:—

	Minimum.	Maximum.	Mean.
Potash,	17·09	33·25	24·67
Soda,	8·60	11·18	9·70
Lime,	17·31	27·55	22·0
Magnesia,	1·90	4·10	3·05
Ferric oxide,	·33	·76	·53
Phosphoric acid,	27·04	29·13	28·45
Sulphuric acid,	...	...	·30
Chlorine,	9·87	16·96	14·28

The chlorine is in combination with the alkalies, the iron, and the earths as phosphate, as well as the potassium oxide. So that the mineral constituents of cows' milk are, phosphate of potash, phosphate of lime and magnesia, common salt, and a trace of phosphate of iron. Other mineral inorganic constituents have been found in small quantity. If sufficient milk be used, it is not difficult to obtain a fluorine reaction, and since fluorides form an essential constituent of the teeth, it is easy to see their importance. A minute quantity of sulphuric acid as sulphates exists in milk, averaging from ·05 to ·08 grm. per kilogramme; and it has also been asserted by G. Musso, that milk contains a sulphocyanate. This assumption was based on the following experiment:—15 litres of milk, freed from caseine, fat, and albumen, were neutralised by baryta water, and evaporated to a syrup, and the syrup extracted with absolute alcohol; the alcoholic extract

dissolved in water and treated with zinc and sulphuric acid, yielded some hydric sulphide; and subsequent treatment yielded from 6 to 21 mgrms. of barium sulphate per kilogramme.* The experiment appears to the author as hardly conclusive of the presence of a sulphocyanate, and requires further investigation.

Nadler has ascertained that neither cows' nor goats' milk contains any iodine: he used for the research 6 litres of cows' milk and 3 of goats' milk.† Minute traces of copper have been found in milk; but lead, arsenic, and all other metals, save iron, are absent.

§ 118. *Other Constituents of Milk.*—In 1864, E. Millon and Commaille, after coagulating and separating the caseine and albumen, obtained a precipitate from the yellow whey by means of a solution of mercury nitrate. This precipitate was white, amorphous, and became slightly red on drying; it was insoluble in water, alcohol, and ether. The precipitate was washed with water, then with alcohol, and finally with ether, and after drying weighed.

	grms.
Cows' milk yielded . . .	2·9 to 3·4 per litre.‡
Goats' milk ,, . . .	1·52 ,,
Sheeps' milk ,, . . .	2·53 ,,
Asses' milk ,, . . .	3·28 ,,
Woman's milk ,, . . .	2·77 ,,

To this body they ascribed the following formula—$C_{30}H_{31}N_5O_{18}$, $HgO + HgO$, NO_3, and gave it the name of *Lacto-proteine*. In 1879, the author studied this body and decomposed it, and came to the conclusion that lacto-proteine, as a single definite substance, had no existence; but that the mercury precipitate was composed of two substances standing between albuminoids and alkaloids, to which the names of *galactine* and *lactochrome* respectively were ascribed. With these substances are precipitated small portions of albumen, which may have escaped precipitation, and traces of urea.

The method of separation adopted by the author is as follows: The caseine and albumen are separated in the manner described at p. 241; the yellow whey is then precipitated by a solution of nitrate of mercury, of about the same strength as that used for estimation of urea;§ the dense flocculent precipitate is then, after

* *Berichte der Deutschen Chemischen Gesellschaft*, xi., p. 154, 1878.

† Ueber den angeblichen Iodgehalt der Luft und verschiedener Nahrungsmittel. *Journal für Praktische Chemie*, 99, p. 198.

‡ Nouvelle Substance contenue dans le Lait. Extrait d'une Note de MM. E. Millon et Commaille. *Comptes Rendus*, 59, p. 301, 1864.

§ The ordinary solution for the estimation of urea is made by dissolving

AVERAGE COMPOSITION OF HEALTHY COWS' MILK.

			Parts per cent. by weight.
Milk-fat	Olein	1·477	3·50
	Stearin and Palmitin	1·750	
	Butyrin	0·270	
	Caproin, Caprylin and Rutin	0·003	
Caseine			3·98
Albumen			0·77
Milk-sugar			4·00
Galactine			0·17
Latochrome			undetermined
Amorphous, bitter principle (glucoside ?) $C_{18}H_{18}O_{24}$	substances precipitated by tannin		0·01*
Crystalline principle, $C_2H_6O_{10}$			undetermined
Lactic acid			Perhaps absent in milk in the udder, but by the time an analysis can be made, always present from ·01 per cent.
Alcohol			traces always present
Odorous principle, oil of milk?			undetermined
Urea			traces, such as ·0001 per cent. nearly always present.
Kreatinine			traces (Commaille).
Ash	K_2O	0·1228	0·70
	Na_2O	0·0868	
	CaO	0·1608	
	Fe_2O_3	0·0005	
	P_2O_5	0·1922	
	Cl	0·1146	
	MgO	0·0243	
Fluorine			very minute traces.
Sulphuric acid in combination			·005
Sulphocyanates			?
Water			86·87

GASES OF MILK.

§ 122. The author has investigated recently the gases contained in milk. Various samples of milk were clamped on to a mer-

* Mean of four determinations only.

curial pump, and the whole of the gas which they yielded pumped out and received in tubes, whence the gas was transferred to a gas apparatus and analysed. A litre of new milk, while fresh and warm from the cow, connected in this way to the pump, yielded 1·83 cc. of gas, which on analysis had the following composition :—

	cc.	Per cent.
Carbon dioxide, CO_2,	·06	3·27
Nitrogen, N,	1·42	77·60
Oxygen, O,	·35	19·13

The proportion of oxygen to nitrogen was therefore nearly as 1 : 4. Another litre of good Devon commercial milk, on being subjected to the same process, yielded 3·468 cc. of gas, the percentage composition of which was :—

	Per cent.
Carbon dioxide, CO_2,	60·47
Nitrogen, N,	30·21
Oxygen, O,	9·30

This sample had been standing at a temperature of 15° for some hours; hence the diminution of oxygen and the increase of carbon dioxide. Various other similar experiments were made, with the result of establishing the fact that a litre of fresh milk yields to the Sprengel pump from 1 to 3 cc. of gas, in which there is always a certain percentage of carbon dioxide, and in which the relation of the nitrogen to the oxygen is very similar to the relation that exists in the air dissolved in water; but that fermentation, at any temperature in which fermentation is possible, at once commences, when the lactic ferment begins to use up the oxygen, and ultimately carbon dioxide is the only gas which can be obtained. This evolution of carbon dioxide is slow but continuous, and it seldom reaches any considerable amount. The author has kept milk for months in bottles provided with a tube dipping under mercury, but only when the temperature was from 18° to 20° was the tension of the gas sufficient to cause it to be evolved without the aid of a Sprengel pump. As an example of this continuous fermentation, one of the experiments may be cited :—100 cc. of milk in which fermentation had begun, were suitably clamped to a Sprengel pump: on the first day there was a small percentage of nitrogen and a little oxygen; and on the second day a trace of oxygen; but on the succeeding days the gas consisted wholly of carbon dioxide, as follows :—

1st day,	1·123 cc. of CO_2
2nd day,	5·086 ,, ,,
3rd day.	19·540 ,, ,,
4th day,	7·621 ,, ,,
5th day,	7·370 ,, ,,
6th day,	9·023 ,, ,,
7th day,	1·780 ,, ,,
15th day,	21·350 ,, ,,
19th day,	4·370 ,, ,,

Giving a total of 77·263 cc. of carbon dioxide in 19 days, the temperature ranging between 14° and 19°·5. Milk previously deprived of dissolved air by the Sprengel pump, then confined over mercury and submitted to an atmosphere of oxygen, rapidly absorbs the oxygen, the place of which is taken by carbon dioxide, provided the temperature is a fermentation one—that is, above 9° and below 60°. This continuous absorption of oxygen was well shown in an experiment of the author's, in which a litre of milk was submitted to the action of a Sprengel pump, and in which it was found there was a continuous slow diffusion of air through the india-rubber connections. It has long been shown by Graham, that air thus finding its way through the minute pores of thick rubber is very highly oxygenised; yet all oxygen rapidly disappeared from the gas, and after the second day pure nitrogen and carbon dioxide could alone be obtained :—

1st day, 6·732 cc. of gas.

	Percentage composition.
Carbon dioxide,	55·392
Nitrogen,	33·780
Oxygen,	10·828

Ratio of oxygen to nitrogen as 1 to 3 nearly.

2nd day, total gas, 7·2 cc.

Carbon dioxide,	49·73
Nitrogen,	49·73
Oxygen,	·54

3rd day, 4·863 cc.

Carbon dioxide,	61·06
Nitrogen,	38·94

4th day,—

Carbon dioxide,	87·98
Nitrogen,	12·02

	Percentage composition.
5th day,—	
Nitrogen,	91·52
Carbon dioxide,	8·48
7th day,—	
Nitrogen,	46·62
Carbon dioxide,	54·58

"FORE" MILK.

§ 123. If an animal is fractionally milked—that is, the whole of the milk received into three or four different vessels—it will be found that, on analysis, the several portions exhibit some difference of composition, more observable in the last and the first, than in the intermediate portions. This difference mainly affects the fat, the first portions of the milk yielding, as a rule, but little fat, while the latter portions, called "strippings" (in speaking of cows' milk), contain an excess of milk-fat. Thus, in a Devon cow milked in this way for the purpose of analysis, the writer found the two extreme portions to have the following composition:—

	Fore Milk.	Strippings.
Specific gravity,	1·0288	1·0256
Milk-fat,	1·166	5·810
Caseine,	2·387	4·304
Albumen,	1·830	·975
Galactine,	·381	·545
Milk-sugar,	3·120	3·531
Ash,	·797	·895
Water,	90·319	83·940
Common salt in ash,	·340	·267

In another experiment a Guernsey cow yielded the following:—

	Fore Milk.	Strippings.
Specific gravity,	1·040	1·023
Milk-fat,	·357	5·946
Caseine,	4·708	3·435
Albumen,	·451	·860
Galactine,	·267	·156
Milk-sugar,	4·943	5·280
Ash,	·874	·929
Water,	88·400	83·394
Common salt in ash,	·100	·098

Dairymen are perfectly aware of the poorness of fore milk in fat, and more than once fraudulent milkmen have endeavoured

to defend themselves by having recourse to the strange expedient of partially milking a cow before such functionaries as aldermen or policemen, and delivering with all formalities the sample to be analysed. The analyst, not knowing its history (for in such cases it is transmitted as an ordinary commercial mik), and finding it on analysis deficient in fat, certifies accordingly, and until the matter is explained suffers in reputation. Such tricks have during the last few years been rather common, but so fully exposed that they are not likely to re-occur.

This difference in the first and last milkings is not confined to cows' milk, but has also been observed in the milk of other animals. Peligot had an ass milked in three successive portions, and found as follows :—

	1	2	3
Milk-fat,	·96	1·02	1·52
Milk-sugar,	6·50	6·48	6·50
Caseine,	1·76	1·95	2·95
Total solids,	9·22	10·45	10·97
Water,	90·78	87·55	89·03

Reiset* has also found a considerable difference in the percentage of total solids in human milk in fractions taken before the child was applied to the breast and after.

	Before Suckling.	After Suckling.
1.	10·58	12·93
2.	12·78	15·52
3.	13·46	14·57

It has been considered that this difference is merely due to the effect of a physical cause; that, in short, as regards cows' milk, the milk already secreted is in the same state as if it stood in a vessel, and the fat rising to the top is, of course, drawn last. This explanation cannot be altogether true, for the same phenomenon is observed in human milk, and here the breasts are horizontal, or nearly so. It is more probable that during the act of milking secretion goes on, and it would seem that the fatty contents of the milk-producing cells are set free before the more watery and albuminous. Hence, the strippings are, as the most recent portions of the whole secretion, rich in fat. This view is supported by an experiment of Reiset, in which it was proved that the longer the time elapsing between the partial milkings, the less the percentage of solids.

* J. Reiset: *Annales de Chimie et de Physique*, 3, ser. xxv., 1849.

HUMAN MILK.

§ 124. Woman's milk has been long an object of research, and numerous analyses of it are scattered through scientific literature. These analyses, in their quantitative results, show considerable discrepancies, so that we must either adopt the supposition that human milk is very variable, or, what is more probable, that the samples taken did not represent the average secretion. From experiment, the author has come to the conclusion that it is impracticable with any mechanical appliances to obtain a complete sample of human milk. In civilised life the nervous system assumes such a high and delicate state of organisation, that the secretion is far more dependent on the presence and contact of the offspring than among animals. Hence, samples of human milk taken by breast pumps, or other exhaust apparatus, can only be considered partial samples; and a study of partial sampling in the case of cows' milk (p. 217) has taught us how very widely the quantities of the fatty constituents in such samples differ from one taken from the whole bulk. Woman's milk contains milk-fat which has not been obtained in quantities sufficient for accurate investigation, and a knowledge of its exact composition is still a desideratum. It, however, certainly contains butyrin, for the author has succeeded in isolating a sufficient quantity of butyric acid from saponified human milk-fat to identify it satisfactorily. Milk-sugar, caseine, albumen, galactine, and a colouring-matter, with mineral substances, are also constituents of woman's milk. The caseine, like that of the ass, is peculiar in not separating in flocculent masses by the processes recommended at p. 241, and the analyst is under the necessity of adopting a different process (see p. 242). This difference is all-important; for in artificial feeding with cows' milk, as soon as the milk reaches the stomach, the milk, in popular language, "curdles," and is often rejected by vomiting. One of the earliest exact analysis of human milk was made by Meggenhofen* in 1826. His treatise scarcely appears to be known, yet it contains pretty well all that is known of the composition of human milk. The total solids of human milk Meggenhofen determined from twelve samples, the highest of which is 13·38, and the lowest 9·25 per cent., the mean being about 12 per cent. Probably for the first time Meggenhofen determined the albumen separately from the caseine, and also weighed "*materiæ animalis tinctura gallarum animalis precipitatæ.*" His view of the composition of human milk may be fairly stated thus—

* *Dissertatio Inauguralis Indagationem Lactis Muliebris Chemicam.* C. Aug. Meggenhofen. Frankfort, 1826.

	Per cent.
Milk-fat,	2·90
Caseine,	2·40
Albumen,	·57
Albuminoid precipitated by gallic acid,	·10
Sugar,	5·87
Ash,	·16
Water,	88·00

According to the writer's own experiments on human milk, and the quantitative analysis of samples taken as fairly and completely as can be done, it has the following composition:—

		Per cent.
Milk-fat,		2·90
Caseine,		2·40
Albumen,		·57
Galactine,		·10
Sugar,		5·87
Ash,		·16
Water,		88·0
Total solids,	12·0	
Solids not fat,	9·1	

With regard to other constituents, urea is often present; there is also an odorous principle. Human milk decomposes similarly to cows' milk, and yields similar gaseous and other products.

§ 125. *Milk of the Ass.*—The author has recently had an opportunity of investigating the milk of the ass. This milk was obtained under his personal superintendence from asses kept and fed in London dairies for the purpose of supplying the demand that still exists for asses' milk. The animals were on a uniform diet of bran, hay, and oats. The yield of each milking was carefully noted, and the ass in each case milked dry. It would appear that the milk of the ass under these circumstances has a very uniform composition, the differences observed being quite unimportant. The yield for commercial purposes appears not to exceed 3 pints, and to average about 2½ pints daily. More than this is doubtless secreted, but some of it is used by the foal. In no case did a single milking yield half a litre (three-fifths of a pint), but usually between 300 and 400 cc.

The mean composition of asses' milk is as follows:—

		Per cent.
Milk-fat,		1·02
Caseine,		1·09
Albumen,		·70
Galactine,		·10
Sugar,		5·50
Ash,		·42
Water,		91·17
Total solids,	8·83	
Solids not fat,	7·81	

The fat contains 5 per cent. of butyric acid, equal to 6·6 per cent. of butyrin; it is probably very similar to butter fat. After the precipitation of caseine, albumen, lactochrome, and galactine, there yet remain principles precipitable by tannin. As in human milk, the caseine is not readily precipitated but remains suspended in a state of fine division, however far lactic fermentation may have progressed.

§ 126. *Milk of the Goat.*—The milk of the goat, as a rule, contains more cream than that of the milk of the cow, and rather less albuminous matter.

Its average composition is as follows:—

		Per cent.
Milk-fat,		4·20
Caseine,		3·00
Albumen,		·62
Galactine,		·08
Milk-sugar,		4·00
Mineral constituents,		·56
Water,		87·54
Total solids,	12·46	
Solids not fat,	8·26	

§ 127. *Milk of the Mare.*—The milk of the mare closely resembles in its constituents the milk of the cow: the caseine, the sugar, and the fat being very similar, if not identical. M. J. Duval* asserts that he has discovered in the milk of the mare a new acid, to which he has given the name of equinic, and which crystallises in groups of little needles; it is not volatile without decomposition, in odour fragrant. It is combined with a base volatilised by heat, which the author considers a base of the ammonia type. Its reactions with silver nitrate, ferric chloride and auric chloride distinguish it from hippuric acid. No analyses are, however, given.

The mean composition of mare's milk is as follows:—

		Per cent.
Milk-fat,		2·50
Caseine,		2·19
Albumen,		·42
Galactine,		·09
Sugar,		5·50
Mineral constituents,		·50
Water,		88·80
Total solids,	11·2	
Solids not fat,	8·7	

* *Comptes Rendus*, t. 82, 419, 1876.

MILK OF OTHER MAMMALS; LACTESCENT PRODUCTS OF BIRDS AND PLANTS.

The following Notes on the Composition of the Milk of other Mammals, &c., may be found useful for comparative purposes.

§ 128. *Milk of the Sheep.*—Sheeps' milk is remarkable for its high specific gravity, and the large amount of solid matter which it contains; the specific gravity ranges from 1038 to 1041, and the total solids may rise as high as 19 per cent. The average composition is as follows:—

		Per cent.
Milk-fat,		5·30
Caseine,		6·10
Albumen,		1·00
Galactine,		0·13
Milk-sugar,		4·20
Ash,		1·00
Water,		82·27
Total solids,	17·73	
Solids not fat,	12·43	

The caseine behaves similarly to the caseine of cows' milk, and separates easily by dilution, acidulation with acetic acid, &c. (see p. 241.) The fat yields 5 per cent. of its weight of butyric acid, and is probably of similar composition to the milk-fat from cows' milk.

§ 129. *The Milk of the Camel.*—Chatin has analysed the milk of the camel. He describes* it as perfectly white in colour, and possessing globules smaller but more numerous than those in cows' milk, the diameter being on an average one-half. Specific gravity, 1·042. It appears to be rather richer in milk-sugar and caseine than cows' milk. Dragendorff† has also analysed camels' milk, and gives the following figures:—

	Per cent.
Albuminoids,	3·84
Fat,	2·90
Milk-sugar,	5·66
Ash,	·66
Water,	86·94

§ 130. *Milk of the Llama.*—Doyère‡ has analysed the milk of the llama. The mean of his three analyses is as follows:—

	Per cent.
Milk-fat,	3·15
Albuminoids,	·90
Milk-sugar,	5·60
Ash,	·80
Water,	89·55

§ 131. *Milk of the Hippopotamus.*—There are few opportunities of analysing

* Sur le Lait de la Chamelle à deux Bosses, par. M. Chatin. *Journal de Pharmacie et Chemie*, t. i., 4 ser., p. 264.

† *Zeitschrift f. Chemie*, 1865, s. 735.

‡ *Ann. de l'Inst. Agrom.* 1852, p. 251.

the milk of this enormous animal, as it is fierce when it suckles its offspring. A sample of the milk was, however, investigated by Gunning.* He describes it as of an acid reaction, and under the microscope showing larger globules than that of other animals. The young hippopotamus sucks under water, and can remain there for a much longer time than the adult animal. The secretion of milk is excessive in quantity, and escapes from the distended teats in streams, which make the water around the animal quite opaque. Its general composition appears to be as follows :—

	Per cent.
Milk-fat,	4·51
Milk-sugar, with a small portion of albuminoid substance,	4·40
Salts,	·11
Water,	90·98

§ 132. *Milk of the Sow.*—The mean of eight analyses collected by König† of sow's milk, is as follows :—

		Per cent.
Milk-fat,		4·55
Albuminoids,		7·23
Milk-sugar,		3·13
Ash,		1·05
Water,		84·04
Total solids,	15·90	
Solids not fat,	11·41	

There are also two analyses of the milk of a sow investigated by Filhol and Joly; the animal was fed on horse-flesh, a diet far from natural; under this diet was secreted a highly albuminous fluid, containing but little sugar. Specific gravity 1·044.

	Per cent.	
Albumen,	[illegible]	21·0
Fat,	6·6	5·4
Sugar,	0·5	1·2
Extractives and salts,	3·01	4·3
Water,	77·0	68·1
Total solids,	23·0	31·9
Solids not fat,	16·4	26·5

§ 133. *Milk of the Bitch.*—The milk of the bitch is highly charged with albuminous solids, and is of a specific gravity ranging from 1·034 to 1·036. It has been investigated by Simon, Dumas, Filhol and Jolly, Talmatescheff, Bensch, Scubotin, and others, with the following mean results :—

		Per cent.
Milk-fat,		9·57
Caseine,		5·53
Albumen,		4·38
Milk-sugar,		3·19
Ash,		·73
Water,		76·60
Total solids,	23·46	
Solids not fat,	13·83	

* *Gazetta Chim. Italiana*, 1871, p. 255.
† *Op. cit.*

§ 134. *Milk of the Cat.*—The milk of the carnivora generally has the peculiarity of having the milk-sugar almost entirely replaced by lactic acid, and hence the milk invariably possesses an acid reaction. An analysis of the milk of a cat by Commaille is as follows. The milk was taken twenty-four hours after kittening; it was feebly acid:—

		Per cent.
Milk-fat,		3·333
Caseine,		3·117
Albumen,		5·964
Lacto-proteine,		·467
Lactose and organic acids,		4·911
Ash,		·585
Water,		81·623
Total solids,	18·377	
Solids not fat,	15·044	

The ·467 would correspond to about ·25 of galactine.

§ 135. *Milk-like Secretions of Birds and Plants.*—It is usually held that mammals alone secrete milk, but this is by no means certain; for during the latter portion of the incubation-period, as well as more profusely for a little while after the young birds are hatched, the pigeon secretes a nutritious albuminous fluid in her crop, which is supposed to be used for the purpose of feeding the young birds. According to Lecomte's analysis this secretion contains,

Caseine and salts,	23·23
Fat,	10·47
Water,	66·30

Such milk-like secretions are by no means confined to the internal mucous membranes of birds. Jonge* has made a most valuable research on the secretion of the glands known to anatomists as *Glandula urophygii*, situated at the tail of the common goose. The secretion was obtained in sufficient quantity for a complete qualitative and quantitative analysis, and although the analysis was not quite so complete as if a larger quantity had been obtainable, it fairly shows that there is a considerable analogy between milk and this secretion, the most marked difference being that no trace of milk-sugar could be found. The analyses of two samples were as follows:—

	1.			2.		
Total solids,			391·93			415·34
Water,			608·07			584·66
Albumen and nuclein,	179·66			127·63		
Compounds insoluble in absolute ether,	186·77			247·08		
Alcoholic extract,	10·90			18·31		
Water extract,	7·53			11·31		
Ash,	7·07	Sol.	3·71	11·01	Sol.	7·71
		Insol.	3·36		Insol.	3·36

* "Ueber das Secret der Talgdrüsen der Vögel und sein Verhältniss zu den fetthaltigen Hautsecreten der Saugthiere, insbesondere der Milch," Von D. de Jonge. *Zeitschrift für Physiol. Chemie*, Von F. Hoppe-Seyler. Strasburg, 1879.

In ether extract,	1	2
Cetyl-alcohol, . .	74·23	104·02
Oleic acid, . . .	6·48	...
Lower acids, . . .	3·73	14·84
Lecithin, . . .	2·33	...

In the vegetable kingdom, numbers of trees or plants yield a white fatty secretion, popularly called milk, though, as a rule, such fluids have no right to this title, being totally different in composition and properties. A very remarkable exception to this assertion is, however, met with in the "milk tree" (*Brosimum galactrodendron*), to be found in Central America. This tree, on incision, yields an abundance of a thickish feebly acid fluid, coagulating on exposure to the air. M. Boussingault has recently analysed this juice, and considers it perfectly analogous to ordinary milk, since it contains a fatty principle, an albuminous principle, a sugar, and phosphates. The exact composition of these different matters has, however, not been determined. Boussingault's general analysis is as follows:—

Fatty saponifiable matters, ...	35·2
Sugar, and substances analogous, . . .	2·8
Caseine, albumen, ...	1·7
Earths, alkalies, phosphates, . . .	·5
Substances not estimated, ...	1·8
Water, ...	58·0

This milk is used largely as a food in the regions where the tree grows.

ABNORMAL MILKS.

§ 136. Milk which deviates from the natural secretion, the animal suffering from no disease, and milk secreted under unnatural conditions, may be conveniently classed as "abnormal." (Milk derived from the unhealthy will be considered in another section.) Instances of *healthy* cows giving milk differing essentially from ordinary milk are very few. One such, however, is recorded by Mr. Pattinson, who analysed the milk of a roan cow, which only gave 2 per cent. of albuminoids, and yielded no less than 4 grms. per litre of common salt. The animal is stated to have been in good health.

The newly-born human infant almost constantly secretes a fluid in the mammæ, and adult males have not only secreted milk, but that in abundance enough to suckle. Females also, both human and animal, occasionally secrete milk without having been previously pregnant. With regard to the milk secreted by infants, there is some doubt about its real nature. Kölliker does not view it as a true milk, but considers its appearance connected with the formation of the mammary glands. Sinety, on the other hand, upon anatomical grounds, considers it a true lacteal secretion. It probably is a sort of imperfect milk loaded with leucocytes, and this is the more likely, as Billard (*Traité des Maladies des Enfants nouveau nés*, 3me edition, 1837, p. 717) notices that it frequently ends in abscess.

Schlossberger gives an imperfect quantitative analysis of a sample of

milk,* obtained by squeezing the breasts of a newly-born infant—a male. In the course of a few days about a drachm was obtained. The following was the result of the analysis:—

	Per cent.
Water,	96·75
Fat,	·82
Ash,	·05
Caseine, sugar, and extractives,	2·83

Sugar reaction strong.

The most complete analysis we yet possess of such milk is one by V. Gesner, which is given in the following table with other less perfect analyses:—

	1†	2‡	3§
Milk-fat,	1·456	·82	1·40
Caseine,	·557	...	2·80
Albumen,	·490	...	
Milk-sugar,	·956	...	6·40
Ash,	·826	·05	
Water,	95·705	96·30	39·40
Total solids,	4·295	3·70	10·60

Jolly and Filhol have recorded the case of an old lady, 75 years of age, who suckled successfully her grandchild.‖ Similar instances have been recorded in dogs, and we fortunately possess one or two analyses which show that the fluid is certainly milk. Thus Filhol and Jolly give the following analysis of the milk derived from a bitch which had no connection with a male:—

Specific gravity,	1·069
Total solids,	29·00
Fat,	2·20
Sugar,	·32
Albumen,	23·20

The ash, on analysis, gave the following percentages in 100 parts:—

Chloride of sodium,	65·10
Chloride of potassium,	3·88
Calcic phosphate,	27·75
Sodic phosphate,	1·40
Sodic carbonate,	1·87

Traces of magnesic and sodic phosphates.

Men before now have suckled children. Humboldt¶ relates the case of Francisco Lozano, whom he saw, and whose case he carefully investigated; and it appears established that this man did secrete from his breasts a nutrient fluid on which his infant son lived for many months, it is said, indeed, a whole year. The curious in such matters may consult the references given in the footnote for additional cases.**

* Untersuchung der sogenannte Hexenmilch, J. Schlossberger, *Annalen der Chemie u. Pharmacie*, b. 87, 1852.

† *Jahrb. f. Kinderkrankheiten, N. F.*, Bd. ix., §160.

‡ Schlossberger u. Hanff, *Ann. Chem. Pharm.*, Bd. xcvj., p. 68.

§ Gabler u. Quevenne, *op cit.*

‖ "Recherches sur le Lait," iii., Bruxelles, 1856.

¶ Humboldt: "Voyage aux Régions Equinoxiales du Nouveau Continent."

** Robert, Bishop of Cork: Letter concerning a Man who gave Suck to a Child, *Phil. Trans.*, 1741, No. 461, t. xli., p. 813. Franklyn: "Narrative

Instances have also been known of a like kind among animals. Schlossberger has analysed the milk derived from a he-goat (*Annalen der Chemie u. Pharmacie*, 1844):

Milk-fat,	26·50
Caseine, with salts soluble in alcohol,	9·60
Sugar, with salts soluble in alcohol,	2·60

The ash was ·782 per cent.—viz., ·325 soluble in water, ·457 insoluble. Occasionally the female mammæ after confinement has continued to yield milk, although the infant has either been dead or nourished otherwise. In such cases the milk deviates from its normal composition, and is, for the most part, highly albuminous. In a case of this kind recorded by Filhol and Joly,* three analyses of the milk were made as follows, at different dates, about a week apart:—

	1.	2.	3.
Specific gravity,	1·039	1·025	1·023
Total residue,	21·50	18·30	18·63
Milk-fat,	5·00	6·15	7·80
Sugar,	2·19	1·27	3·50
Albumen,	12·96	9·00	5·65
Extractives and salts,	1·35	1·88	1·68
Water,	78·50	81·70	81·37

Caseine was entirely absent.

The composition of the ash was as follows:—

	Per cent.
Chloride of sodium,	73·10
Chloride of potassium,	traces.
Calcic phosphate,	23·40
Sodic phosphate,	·80
Sodic carbonate,	1·89
Magnesic and ferric phosphates,	·81

GENERAL EXAMINATION AND ANALYSIS OF MILK.

§ 137. The general examination and analysis of milk may be conveniently treated of under the following heads:—

I. Microscopical examination of milk.

II. Analytical processes, more particularly for the purposes of the food-analyst.

A. General analysis of milk.

(*a.*) Specific gravity.

(*b.*) Total solids.

(*c.*) Extraction of milk-fat.

(*d.*) Extraction of milk-sugar.

(*e.*) Albuminoids and ash.

of a Journey to the Shores of the Polar Sea," 1819, p. 157. Cobbold: Milk from the Male Mamma, *Monthly Journal of Med. Science*, 1854; t. xviii., p. 271. Morgagni: *Adversaria Anatomica Omnia* (*V. Animadversio*, i., p. 3).

* *Comptes Rendus*, t. xxxvi., p. 571. 1853.

B. Various methods proposed for extracting the milk-fat.
   (1.) Solvents for fat.
   (2.) Soxhlet's process.
   (3.) Extraction by ether, acting on alkaline milk.

C. Various other methods of milk analysis.
   (1.) Drying in a vacuum.
   (2.) Direct determination of the water.
   (3.) Absorption of water by dehydrating agents.
   (4.) Ritthausen's copper process.
   (5.) Müller's process.
   (6.) Clausnizer and A. Mayer's process.

III. Special details as to the more exhaustive and scientific analysis of milk.
   (1.) Analysis of the milk-fat, and examination of the ethereal extract.
   (2.) Extraction of the milk-sugar.
   (3.) The ash.
   (4.) Estimation of albumen.
   (5.) Isolation of galactine.
   (6.) Isolation of the principle precipitated by tannin.
   (7.) Estimation of urea.
   (8.) Estimation of alcohol.
   (9.) Volatile acids.
   (10.) Estimation of the total acidity of milk, and estimation of lactic acid.
   (11.) Detection of metals in milk.

I. Microscopical Examination of Milk.

§ 138. A mere chemical analysis is incomplete and insufficient in itself, and should in all cases be preceded or supplemented by a careful and painstaking microscopical examination. Normal milk, viewed under the microscope, presents for the most part a multitude of fat globules floating in a clear fluid. The globules of human milk measure in diameter from ·002 to ·005 mm.; those in the milk of the cow, from ·00062 to ·00039 inch [·0016 to ·01 mm.] These fat globules are of two kinds. By far the most numerous are evidently drops of fluid fat; but there are occasionally to be seen others which would appear to consist of solid fat, for they are rougher on the surface, and less soluble in ether, characteristics which they lose on warming, becoming like liquid-fat globules. In human milk, and, to a certain extent, in cows' milk, there are also as normal constituents, but in sparse quantity—

(1.) Fatty drops having a half moon-shaped, finely granular substance;

(2.) Clear cells enclosing one or two fatty drops, and an eccentric nucleus;

(3.) Round clear bodies, easily coloured by eosin and picro-carmine. These last Heidenhain considers to be free nuclei.*

In the colostrum, or milk drawn the first few days after parturition, there are present other elements—viz., the so-called "colostrum cells." Some of these consist of a number of small and large fat globules, held together by a hyaline tissue or membrane, swelling on the addition of acetic acid or alkalies, and only slowly coloured by aniline red. There are other granular cells coloured at once by the same reagent. If the milk is taken fresh and warm, and a minute drop examined on a Strecker's warm stage,† and kept at a temperature of 38°, the corpuscles will exhibit amœboid movements, perfectly similar to those which have been noticed in the white corpuscles of the blood. Indeed, it is almost certain that the colostrum cells are no other than the white corpuscles of the blood, infiltrated with milk-fat, for Heidenhain, having injected into the dorsal lymph vessel of the frog a cc. of fresh milk, after 48 hours found the white corpuscles loaded with milk-fat, and in no respect distinguishable from colostrum cells. When the milk has undergone any fermentation, the lactic ferment itself may be identified, and little lumps of caseine may be seen. These are mostly irregular and amorphous, but sometimes they have the appearance of flattened cylinders, and other shapes. In abnormal milk may be detected pus or blood, or sometimes both. If the pus is derived from inflammations within the mammæ, and has been mixed with the milk before milking, the pus cells become infiltrated with milk-fat, and are difficult to distinguish from colostrum granules; but if derived from ulcers on the teats, they have the usual appearance of pus cells. The pus cells, like the colostrum cells, and the mucous corpuscles, are all different forms of white blood-corpuscles [leucocytes], and when placed on the warm stage exhibit amœboid movements. Pus cells, as usually observed, are spheroidal, granular, and colourless, measuring from about 1–2500 to 1–3000th of an inch in diameter. On treatment with dilute acetic acid, the cell clears up, and shows two, three, or four nuclei. Blood, in small quantity, gives a pinkish

* R. Heidenhain: "Handbuch der Physiologie." Herausgegeben von Dr. L. Hermann. Leipzig, 1880.

† In default of Strecker's stage, a plate of copper, having a central aperture and a thick straight wire, some inches in length, may be used. The plate is kept at the desired temperature through heating the wire by means of a spirit lamp.

colour to milk; if a large amount be present, it sinks to the bottom in red flocculent masses, which soon, from being deoxidised by the milk, acquire a tint varying from a red more or less dark, to a shade almost black. In small quantities reliance must be placed on the microscopic appearance of the blood-discs, which are wholly unlike any cell found in normal milk. The red blood-discs of the cow are like those of the human subject—little circular, biconcave, flattened discs, measuring on an average 1-4000th part of an inch. Human blood-discs have an average diameter of 1·3500 inch. By the aid of the micro-spectroscope, the absorption-bands may also be seen. These are, in oxidised blood, two bands between D and E, the one close upon the red being narrower, darker, and better defined than the one nearer to the green; with deoxidised blood, only one band is seen, between D and E. On treating the blood with oxygen, or shaking it up with air, the two bands re-appear. In "*blue*" milks a peculiar fungus has been discovered, and in the milk from animals suffering from foot-and-mouth disease, certain special appearances have also been noted, which are described in the section treating of this disease.

II.—Analytical Processes more Particularly for the Purposes of the Food-Analyst.

§ 139. The early attempts at the analysis of milk have been already detailed.

One of the first accurate processes for the general analysis of milk which the author has been able to find, was published in 1853, by MM. Vernois and A. Becquerel.*

A small quantity [30 grms.] was taken, dried, exhausted with ether, burnt up to an ash; the sugar obtained "*à saccharimètre*" from the whey, the caseine being first separated by coagulation by acetic acid, and then estimated by difference. This process was certainly capable of giving very fair and accurate results, and it is the more curious to note, how many English analysts, even very recently, employed erroneous and clumsy methods.

Mr. Wanklyn, by his work on milk analysis,† revived the more accurate method of using comparatively small quantities for analysis, thus avoiding very considerable error, from the risk of large quantities decomposing by prolonged heating. He advocated the use of platinum dishes, and supported strongly the

* *Comptes Rendus*, t. 36, p. 187, 1853.
† "Milk-Analysis." By J. A. Wanklyn. Lond. 1874.

doctrine of the fairly constant character of the non-fatty constituents of milk, dividing the total milk solids into two divisions: the one, "*milk-fat,*" the other, "*solids not fat.*"

Whatever modifications have been since introduced in the methods for the analysis of milk, the general process is still on the principles advocated by Mr. Wanklyn.

A. *General Analysis of Milk.*

§ 140. By the general analysis of milk is meant merely separation of the milk, by the aid of solvents, into milk-fat, solids not fat, and ash. Such an analysis is the simplest quantitative exercise in practical chemistry, and might profitably be given to students as an easy and pleasant task to render them familiar with ordinary weighings and calculation.

(*a.*) *Specific Gravity.*—The specific gravity is first taken. This may be done with fair accuracy by an hydrometer, and still more correctly by a Westphall's balance (or by the balance described at p. 70), or by a specific-gravity bottle. Bottles holding exactly 50 grms. of water at 15° may be purchased. The bottle is filled with the milk, first brought to the required temperature, by either cooling or heating, as the case may be, and weighed, and the specific gravity obtained by multiplying by ·02; or if a bottle is used which contains no simple multiple of 100 grms. of water, the ordinary equation may be used,—

Weight of water : 1·000 : : weight of milk : specific gravity.

(*b.*) *Total Solids.*—The specific gravity having been obtained, exactly 10 cc. are transferred by means of a pipette to a platinum dish, and submitted to the action of a water-bath, until the contents cease to lose weight; this usually takes from two and a half to three hours. It may be proved by direct experiment, that the results from the use of platinum are far more constant and more speedily obtained than those obtained by the use of porcelain or glass evaporating dishes. The author has invariably found that porcelain gave a higher result than platinum, or, in other words, porcelain is more favourable to the milkman. When the residue is perfectly dry, it is at once weighed, and the results expressed in percentage by weight. The weight of the 10 cc. is known from the specific gravity already taken. Thus, supposing a milk of 1·032 specific gravity to give a total residue from 10 cc. of 1·423 grm.: since the specific gravity has shown that 100 cc. of the milk weighed 103·2 grms., it follows that 10 cc. must weigh 10·32 grms.

Hence, 10·32 grms. have yielded a residue of 1·423 grms., which is (calculating only to the first decimal place) 13·7 per cent.

(*c.*) *Extraction of Milk-Fat.*—On treating this dry residue by ether, or petroleum, a further loss will be perceived when the ether is poured off, and the fat-free residue is first dried and then weighed; and this loss represents the milk-fat.

(*d.*) *Extraction of the Milk-Sugar.*—On now exhausting this residue by weak boiling alcohol, repeatedly filtering the alcoholic fluid, and evaporating to dryness, the milk-sugar, with mineral matters dissolved out by the alcohol, is obtained. This evaporation is best effected in a platinum dish. On drying very carefully, weighing, and then burning the sugar away, the ash is left, and must be weighed and subtracted from the original residue of milk-sugar and ash. The amount of sugar is thus obtained with fair accuracy, always being a little too high.

(*e.*) *Albuminoids and Ash.*—Lastly, the caseine, albumen, and insoluble ash left from these operations may be carefully dried and weighed, and then burnt to an ash. This ash, subtracted from the total weight, gives the percentage of albuminoids, while the ash from this operation, added to the amount of ash from the sugar residue, gives the "total mineral constituents." Thus, in this way, it is quite possible, with care, to make an accurate and satisfactory general analysis of milk by using only 10 cc. In practice, however, it is found far more convenient and accurate to take two or three separate portions for the analysis: for example, 10 cc. for the determination of "total solids" and ash; and 25 cc. for the milk-fat.

The foregoing is a brief sketch of the principles of the proximate analysis of a sample of milk. It will be seen that by the simple use of heat, and the application of solvents, such as alcohol and ether, milk is divided into water, milk-fat, milk-sugar, albuminoids, and mineral matters. It is necessary now to consider more in detail the various processes which have been proposed for effecting, in the most accurate and expeditious manner, this division.

B. *Various Methods Proposed for Extracting the Milk-Fat.*

(1.) *Solvents for Fat.*—The solvents for milk-fat are petroleum, ether, or bisulphide of carbon. Of these the latter is, all things considered, the most suitable, since it has no solvent action on the lactic acid. In quite fresh milks, however, the quantity of lactic acid is so small, that ether may be used. 25 to 50 cc. of milk are evaporated in a flat dish with constant stirring and breaking-up of the caseous films by a glass rod, until the whole

is reduced to a rather coarse granular powder. This powder may be transferred to any simple apparatus in use for the exhaustion of substances by volatile solvents; as, for example, Soxhlet's, described at page 67.

(2.) *Soxhlet's Process.*—F. Soxhlet* is the author of a very ingenious process of milk analysis. This process is based on the fact, that if a measured quantity of milk, alkalised by caustic potash, be shaken up with ether, the ether fully extracts the milk-fat, and, on standing, collects in a clear layer. A small, quite constant, proportion of ether remains in solution in the milk, without retaining any of the fat, and without affecting the result. The amount of the fat dissolved in the ether may be determined by the specific gravity of the ether; the higher the specific gravity the greater the proportion of milk-fat. The details of Soxhlet's method are as follows:

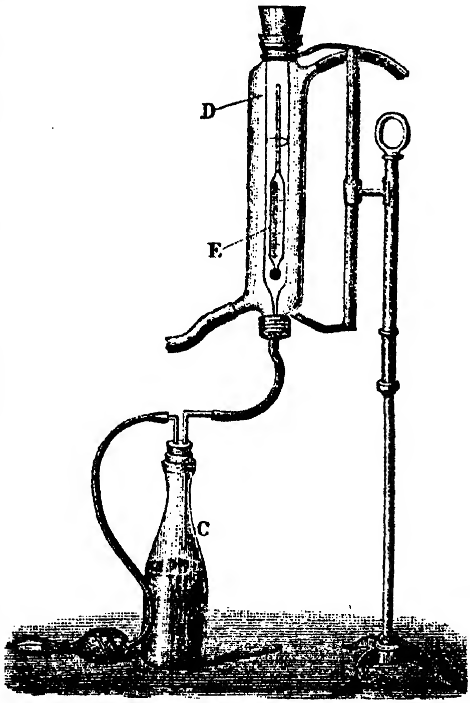

Fig. 26.

The apparatus figured (see fig. 26) is used. C is a measuring flask of 300 cc. capacity, provided with a doubly perforated cork, and connected, on the one hand, with the caoutchouc elastic bulbs figured, which are furnished with suitable valves, and, on the other, with the tube D, which is provided with a water-jacket. This tube carries an areometer, E, which bears a delicate scale of from ·766 to ·743, and it has also a thermometer, divided into thirds of a degree. 200 cc. of milk are measured by means of a pipette, and run into the flask; 10 cc. of potash and 60 cc. of ether, which has been saturated with water at from 16°·5 to 18°·5, are then added, and the whole shaken up in the properly closed flask for a quarter of an hour. The fluid is then allowed to repose until

* *Zeitschrift der Landwirthsch.-Ver. Bayern.* 1880.

the ether rises in a clear layer to the surface. By gently working the caoutchouc bulbs, a sufficient quantity of the fat-laden ether may now be blown up into the tube D, to float the areometer. (It should be mentioned that the tube going through the perforated cork of C, is so arranged as to dip well into the ether, but does not touch the surface of the milk.) The areometer must float freely, and for this purpose there are little prominences on the inside of D, about the middle, for the purpose of keeping the instrument from adhering to the side. When sufficient ether has thus been blown up, it is retained by a pinch-cock, and a cork is fitted into the tube D, to prevent loss by evaporation. The water in the jacket must be of any temperature between 16°·5 and 18°·5. The specific gravity once in this way obtained, and the temperature of the areometer noted, the content in fat of the milk is determined by the annexed table.

If the temperature is exactly 17°·5, then no correction is required; but if it is above that temperature, for every degree, a degree must be added to the gravity; if below, for every degree, a degree must be subtracted. Thus, supposing the areometer marks 58·9 at 16°·8, then, as the difference between 16°·8 and 17°·5 is ·7, subtract ·7 from 58·9, equalling 58·2; or if the observation be 47·6 at 18°·4, then the corrected value is 48·5 (*i.e.*, specific gravity ·74850).

Afterwards the ether is allowed to run back into the flask, and D is washed out with a little ether. The author thinks that the apparatus might be improved by adapting the principles used in the tube figured at p. 69, and floating the ether layer by means of mercury.

(3.) *Extraction by Ether acting on Alkaline Milk.*—The author has recently made some determinations of milk-fat by shaking up milk made very alkaline by soda, in a graduated tube like the one proposed at p. 69. By now expelling by means of the mercury reservoir a known bulk of the ether, and drying it up, the fat is estimated with great rapidity. According to test-experiments the percentage of fat obtained is the same as that by exhaustion methods—to the first decimal place: hence, though not suitable for exact scientific inquiry, it will be found sufficiently accurate for all technical purposes.

C. *Various other Methods of Milk Analysis.*

§ 141. There are other methods of analysing milk:—

(1.) *Drying in a Vacuum.*—The author finds that by putting 5 cc. of milk in a small strong flask, and connecting this flask with

Specific gravity.	Fat. Per cent.	Specific gravity.	Fat. Per Cent.	Specific gravity.	Fat. Per cent.	Specific gravity.	Fat. Per cent	Specific gravity.	Fat. Per cent.
43	2·07	47·7	2·61	52·3	3·16	56·9	3·74	61·5	4·39
43·1	2·08	47·8	2·62	52·4	3·17	57	3·75	61·6	4·40
43·2	2·09	47·9	2·63	52·5	3·18	57·1	3·76	61·7	4·42
43·3	2·10	48	2·64	52·6	3·20	57·2	3·78	61·8	4·44
43·4	2·11	48·1	2·66	52·7	3·21	57·3	3·80	61·9	4·46
43·5	2·12	48·2	2·67	52·8	3·22	57·4	3·81	62	4·47
43·6	2·13	48·3	2·68	52·9	3·23	57·5	3·82	62·1	4·48
43·7	2·14	48·4	2·70	53	3·25	57·6	3·84	62·2	4·50
43·8	2·16	48·5	2·71	53·1	3·26	57·7	3·85	62·3	4·52
43·9	2·17	48·6	2·72	53·2	3·27	57·8	3·87	62·4	4·53
44	2·18	48·7	2·73	53·3	3·28	57·9	3·88	62·5	4·55
44·1	2·19	48·8	2·74	53·4	3·29	58	3·90	62·6	4·56
44·2	2·20	48·9	2·75	53·5	3·30	58·1	3·91	62·7	4·58
44·3	2·22	49	2·76	53·6	3·31	58·2	3·92	62·8	4·59
44·4	2·23	49·1	2·77	53·7	3·33	58·3	3·93	62·9	4.61
44·5	2·24	49·2	2·78	53·8	3·34	58·4	3·95	63	4·63
44·6	2·25	49·3	2·79	53·9	3·35	58·5	3·96	63·1	4·64
44·7	2·26	49·4	2·80	54	3·37	58·6	3·98	63·2	4·66
44·8	2·27	49·5	2·81	54·1	3·38	58·7	3·99	63·3	4·67
44·9	2·28	49·6	2·83	54·2	3·39	58·8	4·01	63·4	4·69
45	2·30	49·7	2·84	54·3	3·40	58·9	4·02	63·5	4·70
45·1	2·31	49·8	2·86	54·4	3·41	59	4·03	63·6	4·71
45·2	2·32	49·9	2·87	54·5	3·43	59·1	4·04	63·7	4·73
45·3	2·33	50	2·88	54·6	3·45	59·2	4·06	63·8	4·75
45·4	2·34	50·1	2·90	54·7	3·46	59·3	4·07	63·9	4·77
45·5	2·35	50·2	2·91	54·8	3·47	59·4	4·09	64	4·79
45·6	2·36	50·3	2·92	54·9	3·48	59·5	4·11	64·1	4·80
45·7	2·37	50·4	2·93	55	3·49	59·6	4·12	64·2	4·82
45·8	2·38	50·5	2·94	55·1	3·51	59·7	4·14	64·3	4·84
45·9	2·39	50·6	2·96	55·2	3·52	59·8	4·15	64·4	4·85
46	2·40	50·7	2·97	55·3	3·53	59·9	4·16	64·5	4·87
46·1	2·42	50·8	2·98	55·4	3·55	60	4·18	64·6	4·88
46·2	2·43	50·9	2·99	55·5	3·56	60·1	4·19	64·7	4·90
46·3	2·44	51	3·00	55·6	3·57	60·2	4·20	64·8	4·92
46·4	2·45	51·1	3·01	55·7	3·59	60·3	4·21	64·9	4·93
46·5	2·46	51·2	3·03	55·8	3·60	60·4	4·23	65	4·95
46·6	2·47	51·3	3·04	55·9	3·61	60·5	4·24	65·1	4·97
46·7	2·49	51·4	3·05	56	3·63	60·6	4·26	65·2	4·98
46·8	2·50	51·5	3·06	56·1	3·64	60·7	4·27	65·3	5·00
46·9	2·51	51·6	3·08	56·2	3·65	60·8	4·29	65·4	5·02
47	2·52	51·7	3·09	56·3	3·67	60·9	4·30	65·5	5·04
47·1	2·54	51·8	3·10	56·4	3·68	61	4·32	65·6	5·05
47·2	2·55	51·9	3·11	56·5	3·69	61·1	4·33	65·7	5·07
47·3	2·56	52	3·12	56·6	3·71	61·2	4·35	65·8	5·09
47·4	2·57	52·1	3·14	56·7	3·72	61·3	4·36	65·9	5·11
47·5	2·58	52·2	3·15	56·8	3·73	61·4	4·37	66	5·12
47·6	2·60								

N.B.—The numbers in the specific gravity column correspond to those on the areometer scale, the number 7 being omitted on account of the narrowness of the stem of the instrument; thus 46 really means ·7460, and so on with the rest.

a second containing strong sulphuric acid, and, lastly, attaching the two flasks to a Lane-Fox mercury pump, the milk solids may be boiled, and the water expelled off at a temperature of about 40°. The solids are perfectly dry in about one hour and a quarter. It was noticed in some test-experiments that in all cases the dry solids obtained in this way were about ·5 per cent. higher than the weight of dry solids in the water-bath—a proof that in all cases drying in the ordinary way entails loss. After the dry solids have been deprived of fat by ether or petroleum, the albumen and sugar may be dissolved out by cold water to which acetic acid has been added. On precipitation of the albumen by boiling, the latter may be collected on a weighed filter, dried, and weighed. On evaporation of the filtrate, the soluble ash, the milk-sugar, and the bodies described at p. 242 are left; on ignition, the difference of weight before and after gives very nearly the amount of sugar. Lastly, the caseine and insoluble ash are obtained from the portion of original milk insoluble in cold water.

(2.) *Direct Determination of the Water.*—In most analyses the water is inferred from the loss; it may, however, occasionally be necessary to estimate it directly. This can be readily done as follows:—5 cc. of milk are placed in a small flask; a piece of tubing is sealed at one end, and graduated into cc.'s; it will only be necessary to mark it at 4·5 and at 5·5, graduating it, between these numbers, into 10ths. The tube is now bent twice at right angles, and connected by a caoutchouc cork to the flask; another narrow tube goes to the mercury pump; the flask is now exhausted of air; and by applying a flame to the connecting tube, the tube is drawn out and sealed. By now plunging the limb of the graduated sealed tube into ice and salt, and gently warming the flask, the milk boils, the water is all condensed in the limb, and the amount can be seen by simple inspection. A somewhat similar method of analysing milk, by a special apparatus, has been recently patented in Germany, by J. Petri and R. Muencke.*

(3.) *Absorption of Water by Dehydrating Agents.*—Another method for the general analysis of milk consists in adding an excess of anhydrous gypsum to the milk, which very rapidly extracts the water; the powder can then be exhausted by ether, and the fat estimated, while, similarly, the sugar may be dissolved out by alcohol. This method for the purpose of estimation of fat and sugar is most decidedly rapid and convenient.

(4.) *Ritthausen's Copper Process.*—Ritthausen† dilutes milk to

* *Deutsche Patentschrift*, No. 7477.

† "Neue-Methode zur Analyse der Milch," and "Ueber ein vom Milch-

twenty times its volume, and adds a solution of copper acetate, 10 cc. = ·0095 CuO [or copper sulphate, 10 cc. = ·2 CuO]. A sufficient solution of KHO or NaHO must also be added, to prevent the separation of basic salt. On filtration, a filtrate separates containing no copper; and may be used for the estimation of sugar by Fehling's solution; the precipitate is dried and exhausted of fat, and ultimately ignited. This method has not come into general use, and is, on the whole, not to be recommended.

(5.) *Müller's Process.*—Alexander Müller* is the author of a method of milk analysis which is ingenious, but it is difficult to see in what way it is superior to other processes more used, either in precision or accuracy. He uses small flasks, the weight of which must not exceed 25 grms., which will hold when full about 60 to 65 cc. In one of these small flasks 6 cc. of the milk are put and weighed; exactly 50 cc. of a mixture of 1 volume absolute alcohol and 3 volumes ether are now added, with special precautions to prevent loss by evaporation. The solvent is allowed to act for twenty-four hours. The precipitate by this time has separated completely, and it is possible to isolate the alcohol-ether contents without filtration. The next process is to obtain exactly 50 cc. of the liquid without loss and without the precipitate. This is effected by connecting the digestion flask by means of a bent tube with a flask which is marked for 50 cc. on the neck. This last flask has a double bored cork, one carrying the connecting tube, the other a tube for the purposes of suction; and the ether-alcohol is carefully sucked over to the mark, gently inclining the digestion flask, &c. Lest the incoming air should carry away any of the alcohol-ether, it (the air) is made to pass first through a few cc. of ether in a third flask. The 50 cc. are evaporated to dryness, and contain fat, with a little milk-sugar and a little common salt. For technical purposes, a correction constant is made for these impurities of about one-quarter per cent.; while for scientific purposes, the fat is taken up again by means of petroleum ether. The residue in the digestion flask contains nearly all the milk-sugar, the mineral constituents, and the albuminoids; it is dried and weighed in the usual way. The fat from the one flask and the solids from the other, when added together, equal the total solids. Müller calculates the caseine by determining the nitrogen, and obtains the ash by acidulating 6 cc. with a little nitric acid,

Zucker verschiedenes Kohlenhydrate in der Kuhmilch," von H. Ritthausen, *Journal für Prak. Chemie*, 15, p. 329, 1877.

* *Zeitschrift für Analytische Chemie*, xx. 189.

heating slowly with a heat that is gradually increased from gentle warmth up to redness.*

(6.) *Clausnizer and A. Mayer's Process.*—An indirect method of estimating milk-fat has been proposed by F. Clausnizer and A Mayer.† They assume that every percentage of "milk solids not fat" raises the specific gravity ·00375, whilst every 1 per cent. of fat lowers the specific gravity ·0010; by therefore first making an accurate determination of the specific gravity, and then drying the solids, the amount of fat can be known by using the following formula—

x = fat,
s = specific gravity,
t = total solids,

then

$$1+(t-x)\ 0{\cdot}00375-s=x\ .\ 0{\cdot}0010;$$

therefore

$$1+t\ 0{\cdot}00375-s=x.\ {\cdot}00475$$

therefore

$$x=\frac{t\ .\ {\cdot}00375+1-s}{{\cdot}00475}$$

For the sake of expedition they only evaporate ·5 cc. of milk.

Summary of the Processes for the Technical Analysis of Milk already described.

What particular procedure an analyst may select to obtain a knowledge of the *general* composition of milk, will mainly depend upon the purposes for which the analysis is required. Where a large number of milks are analysed daily, there is scarcely any more convenient and trustworthy method than to have one or two dozen little platinum dishes (Wanklyn's) fitted into a suitable water-bath, and take the "total solids" and ash in these dishes, while the fat is extracted from another portion by carbon disulphide in a Soxhlet's apparatus, of which half a dozen or more, with attached condenser, should under such circumstances be fitted up permanently. On the other hand, special circumstances may arise rendering some of the newer pro-

* It is necessary to observe that in extracting the fatty constituents by this ether process, when 50 cc. of ether-alcohol are added to 6 cc. of milk, the c. volume is not 56 cc., but 54·3 cc.; therefore, the weighed fat must be multiplied by $\frac{54{\cdot}3}{50}$ in order to obtain the quantity of matters dissolved from 6 cc.

† F. Clausnizer and Adolf Mayer. *Forschungen auf dem Gebiete der Viehhaltung in ihrer Erzeugnisse*, 1879, 265.

cesses enumerated at pp. 234-238 more suitable. If, for example, there should be a dispute about the actual amount of water in a certain milk, it will be more satisfactory to estimate the water by distilling it over in a vacuum, than to determine it solely by the loss.

Again, if it should be desired to gain rapidly some approximate idea of the quantity of fat and total solids in milk, a careful determination of the specific gravity, and determination of the fat by some of the processes at pp. 233, 234, have no small advantages where time is an object. The analyst has, indeed, a great variety of processes to choose from; those detailed may be modified in many ways; they cannot be pronounced of equal value or of equal accuracy; but each possesses certain advantages and certain claims—in this, as in most other things, "the fittest survives," and is adopted.

III. Special Details as to the More Exhaustive and Scientific Analysis of Milk.

§ 142. (1.) *Analysis of the Milk-Fat and Examination of the Ethereal Extract of Milk.*—The milk-fat is seldom analysed, save when met with in commerce as butter. Yet, in the complete examination of milks suspected to be abnormal, it is of some importance to examine the ethereal extract as thoroughly as possible. The ethereal extract should be tested for nitrogenous substances, for phosphorous compounds, and for cholesterine, and finally saponified, and the volatile acids at least estimated. Nitrogenous matters may be assumed to be absent if, on boiling the fat with a strong alkaline lye (proved to be ammonia-free) and distilling, an alkaline distillate is not obtained.

Phosphorus may be tested for by burning up the fat intimately mixed with a mixture of carbonate and nitrate of soda, dissolving the ash, acidifying with nitric acid, and testing with molybdate of ammonia. Any precipitate which occurs is allowed to stand for twelve hours, and is then filtered off, dissolved in dilute ammonia, and precipitated by the ordinary magnesia mixture. Thus, the experiment may be made quantitative as well as qualitative, for the ammonio-magnesia phosphate may be dried, ignited, and weighed. The further analysis of the milk-fat is described in the article on "Butter."

Cholesterine.—Cholesterine is found in many fluids of the body, and is a constant constituent of pus. It is occasionally present in milk. Cholesterine, if present in milk, will be found in the ether extract. The ether having been distilled off, the

fatty residue is dissolved and saponified in boiling alcoholic potash, the alcohol is evaporated from the soap, and to the residue a little water is added, and then the fluid shaken up with ether, which will not dissolve the soap, but will take up any cholesterine that may be present. The ether is carefully removed by a pipette, and any residue found on evaporating repeatedly crystallised from a mixture of alcohol and ether. Pure cholesterine appears under the microscope as thin rhombic plates, melting point about 145°, but should it be impure the melting point is lower than this. It is insoluble in water, in concentrated alkaline solutions, and in dilute acids. A drop of concentrated sulphuric acid, added to a crystal with a very little iodine, causes a play of colours, passing from violet-blue into green, and lastly red.

§ 143. (2.) *Extraction of the Milk-Sugar.*—The milk solids freed from fat are first treated with strong alcohol, which renders the albumen insoluble, then a little water is added, and the liquid, now in effect weak alcohol, boiled for a few minutes. This is filtered, and the process repeated three times. If 10 to 20 cc. of milk is the quantity originally used, then the total filtrate should be at least 70 to 100 cc. This is now evaporated to dryness on the water bath, weighed, and finally ignited. The loss on ignition represents the milk-sugar contaminated with galactine, some lactochrome, and the substances precipitated by tannin. The solvent processes given are sufficient for most purposes; but when scientific accuracy is required, it is best to estimate by copper suboxide. Thus, 25 cc. of milk are diluted with 400 cc. water, and then, to get rid of the fat and albuminoids, treated with 10 cc. of a solution of copper sulphate (strength 69·28 crystallised $CuSO_4$ per litre); 6·5 to 7·5 cc. of a solution of potash is added (the solution must be so proportional in strength that 1 vol. of the alkaline solution will exactly precipitate 1 vol. of the copper solution). After this addition the fluid must still have an acid reaction, and hold some copper in solution. The liquid is made up to 500 cc., and filtered; 100 cc. of the liquid, the strength of which is about one-fourth per cent., is boiled with 50 cc. of Fehling's solution. After six minutes the solution is filtered through an asbestos filter, and the copper oxide reduced to metallic copper in a stream of hydrogen. The following table is used to correct the errors arising from different concentrations of the solutions. For example, if the copper weighs 240 mgrms., the true weight of the sugar is calculated from the number nearest to 240 in the table—viz., 237·5, and so on:—

TABLE XV.

Weight of Copper.	Milk-sugar.	100 parts of Milk-sugar. Precipitate of Copper Oxide.	Reduction Ratio.
Mgrms.	Mgrms.		
392·7	300	130·9	1 : 7·43
363·6	275	132·2	1 : 7·50
333·0	250	133·2	1 : 7·56
300·8	225	133·7	1 : 7·59
269·6	200	134·8	1 : 7·65
237·5	175	135·7	1 : 7·70
204·0	150	136·0	1 : 7·72
171·4	125	137·1	1 : 7·78
138·3	100	138·3	1 : 7·85

§ 144. (3.) *The Ash.*—The ash is estimated in a quantity of milk, which should not exceed 25 cc. It will be found that larger quantities do not at all conduce to accuracy, as the large amount of carbon, with even great care, develops too much heat, and the phosphates are liable to fuse, enclosing little particles of charcoal extremely difficult to burn. With small quantities, however, the milk rapidly burns to an almost white ash. It may be further analysed on the principles laid down at p. 97.

§ 145. (4.) *Estimation of Albumen.*—This is most rapidly done when the milk solids are dried in a vacuum, as described at p. 234, then the albumen may be dissolved out by the aid of cold water, acidulated by acetic acid. If this process is not adopted, the following may be used:—100 cc. of milk are divided into three equal portions. One of these portions is diluted to about four times its volume, and acidified with dilute acetic acid until the caseine coagulates in a flocculent condition; a current of carbon dioxide is now passed through, and the precipitate allowed to subside. The whey is then carefully syphoned off on to the second portion of the milk; more acid, if necessary, is added; the same operation repeated; and this second whey similarly added to the third portion of milk. Finally, the whole of the caseine is collected on a filter, and washed. The result of the process is, that the albumen from 100 cc. of milk is held in solution in about 250 to 300 cc. This solution is now raised to the boiling point, and gently boiled for a few minutes. The whole of the albumen falls down, and is easily collected on a previously dried and weighed filter. This easy separation of the caseine and albumen by acetic acid and carbon dioxide only applies to the milk of the cud-chewers; with human milk, the milk of the horse or of the ass, the process gives no good result:

when treated in the same way, it is true that the caseine appears to coagulate, but it is in a state of such fine division that nearly all of it remains suspended in the liquid, and filtration through paper becomes impossible. From all these a clear filtrate may, however, be obtained by filtration under pressure through a porous cell. The method for this purpose used by the author is to take an ordinary cylindrical, porous earthenware cell, such as are sold for galvanic batteries; to stopper it with an accurately-fitting caoutchouc plug, perforated in the centre; and then, by means of an angle tube and caoutchouc-pressure tubing, to attach it to the mercury pump. The milk is diluted, acidified with acetic acid, and saturated with carbon dioxide as before; the cell is then totally immersed in the dilute acid milk, which for this purpose is placed in a tall beaker; a good vacuum is maintained, and ultimately the whole of the whey passes through, and the caseine may be washed two or three times with water. Besides this very convenient method, there are many substances which will carry down the precipitated caseine mechanically; thus, the author has found that a solution of phosphate of lime in acetic acid may be added to the acid milk; when, on cautiously neutralising with ammonia, the earthy precipitate clears the liquid by its mechanical action.

§ 146. (5.) *Isolation of Galactine.*—A litre of milk is the smallest quantity which can be taken for the isolation of galactine. As in the previous operation, 100 cc. of milk are greatly diluted, the caseine coagulated, and the whey separated by subsidence. This whey is used for the precipitation of a second portion, and the same whey from the second portion for the precipitation of a third, and so on. By this means it is possible to obtain the whey from a litre of milk in a form not too dilute. The albumen may be separated from time to time in the different fractions, or in one concluding operation; lastly, the caseine must be collected and well boiled, and the liquid separated from it by filtration and strong pressure. A solution of nitrate of mercury is now added, and decomposed by hydrogen sulphide, and the filtrate precipitated by lead acetate. The amount of galactine may be estimated from the weight of the lead oxide left on ignition of the lead compound, for it will be found that the complete drying of the lead-galactine is tedious.

§ 147. (6.) *Isolation of the Principles Precipitated by Tannin.*—The whey, now freed from caseine, albumen, galactine, and colouring-matter, but containing mercury nitrate, must be made alkaline, the precipitate filtered off, the liquid saturated with hydrogen sulphide, any precipitate again filtered off, the liquid concentrated to a small bulk and completely precipitated with

tannin. The tannin precipitate is decomposed as before described, p. 213.

§ 148. (7.) *Estimation of Urea.*—The estimation of urea is of some importance, since any disorder interfering with the action of the kidneys throws (as has been well ascertained) an excess of urea on all the secretions of the body. A known quantity of milk, which should not be less than half a litre, is evaporated with constant stirring in very large flat dishes to a granular condition. The fat is next extracted by dry ether, and from the fat-free solids the urea is extracted with other substances by boiling alcohol. The alcoholic solution is evaporated to dryness; and from this dry residue absolute alcohol will extract the urea nearly pure. A litre of milk in its normal state yields about 10 mgrms. Urea must be identified by its properties as follows:—

It is crystalline, crystallising in quadratic prisms, and polarising with a gentle blue colour under the microscope. The crystals should be heated with a little hydrate of baryta in a closed tube to 200° for some hours, when a very definite reaction ensues, ammonia and carbon dioxide being produced. The liquid may be distilled, and ammonia identified by the Nessler test. Carbonate of baryta will appear as a precipitate, and may be readily examined, converted into sulphate, and weighed; 1 part of barium sulphate = ·2574 urea. A convenient method of identifying urea is also to dissolve the crystals in the smallest possible quantity of water, and then to add a drop of dilute nitric acid; the nitrate of urea is precipitated, and can be identified by its microscopic characters. Nitrate of urea crystallises on the rhombic system. The most common appearance is that of large plates, many of which lie one upon the other.

§ 149. (8.) *Estimation of Alcohol.*—A litre of milk, which, if acid, must be neutralised, is placed in a specially constructed, non-tubulated, very capacious retort, provided with a tube a metre in length. This tube is surrounded by a water jacket, through which a continuous stream of cold water runs. The retort tube is pushed through a strong india-rubber stopper, and connected with a small flask holding about 200 cc., and immersed in ice and salt. The india-rubber stopper, by the aid of a second perforation, carries a piece of angle tubing, by which it may be connected with the mercury pump (fig. 7), or, where available, with the ordinary water pump so common in laboratories. The milk is now cautiously raised to the boiling point, and 100 to 150 cc. distilled over. This distillate is redistilled, in the ordinary way, about one-third. All the alcohol is now in a very small compass, and the distillate should be placed in a strong assay flask, and oxi-

dised to acetic acid by heating in a water-bath with from 30 to 70 cc. of an oxidising solution of bichromate of potash and sulphuric acid.* The excess of bichromate is reduced by zinc, some phosphoric acid added, and the acetic acid distilled off by heating the flask (previously attached to an efficient condenser) over a spermaceti bath. On distilling in this way about three times to dryness, each time adding water, the whole of the acetic acid is obtained in the distillate, and may be determined by titration with a volumetric solution of soda. The amount of alcohol to which the acetic acid found is equal may be calculated by the aid of the following table:—

Acetic Acid.	Alcohol.
1,	·7666
2,	1·5332
3,	2·2998
4,	3·0664
5,	3·8330
6,	4·5996
7,	5·3662
8,	6·1328
9,	6·8994
10,	7·6666

The amount of alcohol is seldom of any great importance, and may be considered only of pure scientific interest.

§ 150. (9.) *Volatile Acids.*—Volatile acids may be separated in exactly the same way—viz., by careful distillation in a vacuum, first acidifying the milk by tartaric acid. Acetic acid in small quantities is invariably present in fermented milks; but the distillate of normal, quite fresh milk is neutral. In milks already undergoing decomposition, it is best to dilute the milk slightly, and filter through an earthenware cell, and then distil. Under these circumstances, it is not necessary to distil *in vacuo.*

§ 151. (10.) *Estimation of the Total Acidity of Milk—Estimation of Lactic Acid.*—The total acidity of milk is most conveniently estimated by adding 14 grms. of chloride of sodium to 30 cc. of milk. The caseine coagulates in a few minutes, and the liquid may be diluted, and a fractional portion filtered off, coloured by litmus or any convenient indicator, and titrated in the usual way.†

Estimation of Lactic Acid.—It is of great importance to make an accurate estimation of lactic acid in milk. A method, accurate enough for technical purposes, consists in thoroughly exhausting

* 147 grms. bichromate of potash: 220 grms. of sulphuric acid made up to 1400 cc. with water.

† "Di un metodo pratico per determinare il grado di acidita del latte." A. Pavesi, ed. E. Rotondi. *Gazetta Chimica Italiana*, vol. iv., 1874, p. 194.

the milk of fat and lactic acid by ether, then taking another portion and exhausting it by carbon disulphide, when the difference between the two determinations represents the lactic acid. A more accurate method is as follows :—The milk is dried, exhausted of fat by carbon disulphide, then treated with an alcoholic solution of oxalic acid, filtered, and an excess of hydrated oxide of lead added. Any lactic acid now contained in the fluid will be present in solution as a lactate of lead. Hydrogen sulphide is next passed to saturation into the liquid, which is then filtered, concentrated by evaporation, and boiled with oxide of zinc; on filtration, evaporation, and standing, crystals of lactate of zinc are produced. There are four isomeric lactic acids; that which is obtained from milk is fermentation lactic acid, also termed "ethylene lactic acid." The zinc salt has the composition $2(C_3H_5O_3)Zn + 3H_2O$. It crystallises in four-sided prisms; it is soluble in 6 parts of boiling, 58 of cold water. It is nearly insoluble in hot or cold alcohol. 100 parts of the salt contain 25·8 of zinc oxide. Lactic acid itself may be obtained in a very pure state by decomposing the zinc-salt with hydrogen sulphide, when the acid presents itself as a colourless, strongly acid liquid. A drop of this acid, placed in the author's subliming cell (described in the second volume of this work), and heated very gradually above 200°, gives a white sublimate of lactide, $C_3H_4O_2$, a very characteristic reaction. If the heat is not gradual, this sublimate is not obtained, for it then decomposes into carbon dioxide and aldehyde.

§ 152. (11.) *Detection of Metals in Milk.*—The detection of the minute quantities of heavy metals which may occur in milk in cases, where, for the purpose of experiment, salts of the metals have been administered to animals or women, is best conducted by electrolysis, supplemented by the spectroscope. One of the best ways to do this is the method proposed by Dr. Reynolds.* Four to six rather stout platinum wires, half an inch in length, are made into a bundle by binding with thin platinum wire, and secured by cotton wool into the throat of the stem of a funnel so tightly, that water placed in the funnel filters through in single drops. The milk, previously acidified with nitric acid, and filtered, is placed in the funnel, and a platinum wire, connected with one pole of a battery, inserted in the funnel, so as to be about half an inch distant from the bundle of wire. This bundle is connected with the zinc terminal of the battery—a single Grove's cell is sufficient—and the current is allowed to pass until the whole has filtered through. A very decided metallic deposit

* *Irish Hospital Gazette*, 1873. See also "The Spectroscope in Medicine," by C. A. Macmunn, B.A., M.D. London, 1880.

may be recognised, and examined by ordinary analysis; but should the deposit be scanty or indistinct, two of the short wires are connected with a Ruhmkoff's coil attached to a sufficiently powerful battery. The wires are so adjusted opposite each other as to leave a very short interval between their points, and the succession of sparks allowed to stream between them, is observed by the spectroscope. In this way the spark spectra of the metals arsenic, antimony, mercury, copper, and lead, are easily obtained, and may be identified.*

THE MILK SECRETED BY THE UNHEALTHY.

§ 153. The author has devoted considerable time to the inquiry,—is it possible, by scientific examination, to discover whether a particular sample of milk has been derived from the healthy or from the unhealthy? The result of the analyses and cases shortly to be quoted shows,—(1.) That in the case of the cow, in certain diseases only, the milk constantly deviates from the normal standard; (2.) that the most marked changes are found in *local diseases of the udder or mammary glands;* (3.) that the animal may be labouring under a most mortal and virulent malady, and yet secrete milk which, although differing from the same milk secreted by the same animal when in health, yet, considered in itself, in no way *chemically* differs from healthy milk; (4.) that it is only by biological methods of experiment that such diseased milk can be detected. These remarks apply only to the *composition* of the milk; but if we also regard the *quantity* secreted, then there is in all cases a remarkable difference, for whenever an animal suffers from a sufficient amount of disease to affect its health materially, the diminution in the total quantity of milk is almost invariable.

I. Human Milk.

§ 154. With regard to the milk secreted by women in various maladies, the same remarks apply only to a certain extent; for the human manmary secretion is so dependent on mental influences, that its composition appears readily affected. Vogel gives the following analysis of milk derived from a woman suffering from hysteria, the sample being taken directly after the attack—

* Reference may be made to Boisbeaudran's "Spectres Lumineux." Paris, 1874. A simple method of obtaining the wave length value of any spectroscope scale has been already given in the article on the "Spectroscope" in the present volume, p. 77 *et seq.*

	Per cent.
Milk-fat,	·514
Caseine,	5·000
Sugar,	3·492
Ash,	1·010
Water,	89·984
Specific gravity,	1·032

Deveux* found the milk of a woman who suffered from nervous attacks, when taken in the seizure, to be a transparent viscid secretion like albumen. J. F. Simon† examined the milk of a woman who was suffering from the effects of passion. The secretion was apparently the cause of violent convulsions and diarrhœa in an infant. The milk was acid, and had acquired a peculiar odour, and after a little time developed hydrogen sulphide; or, in other words, the milk had commenced to undergo lactic acid and putrefactive changes in the breast itself. Local affections of the breast, as might be anticipated, interfere with the healthy action of the milk-producing cells. For example, Schlossberger gives the following as the composition of a sample of milk taken from a woman whose breast was considerably enlarged; the fluid was white and thick, and without odour, specific gravity, ·98 to ·99 at 15°:—

	Per cent.
Fatty matter,	8·54
Lactine and extractives,	·75
Caseine,	8·74
Ash,	·41

The fat fused at 33° and solidified at 26°.

II. Cows' Milk.

§ 155. *Aphthous Fever.*—One of the few affections in which it is possible for the investigator to discover an abnormal condition of the milk, and even from the appearance of the fluid to know what particular malady the cow is suffering from, is "*foot-and-mouth disease,*" or "*aphthous fever.*" This is a febrile, highly infectious disease, which has caused of late great ravages among our herds; its most obvious signs are ulcers on the mouth, feet, and teats. Unless the fever is high, the milk is secreted during the whole course of the disease. It presents different (one might almost say, opposite) appearances in different cases; in those where there are ulcers on the teat, either externally or just inside, the pus from these ulcers mixes with the milk, and the analyst finds a high fatty residue, from which cholesterine, nuclein, lecithin, and milk-fat may be separated. If, on the contrary, there are no ulcers and no local affection of the udder, the milk in the more severe cases may be deficient in solids, and especially in milk-fat; nor does it recover its normal composition until about

* *Crell's Chemische Annalen*, vol. 1, p. 369.

† J. F. Simon's "Animal Chemistry," Syd. Soc., 11, 58.

the seventh and eighth days, when the cow begins to improve. The author discovered, in 1876, some peculiar appearances in aphthous milk, an observation since amply confirmed by others. Such milk, observed on the first day by the microscope, presents no remarkable peculiarity; but, on the third day, elongated, highly flattened, highly refractive bodies, ranging in length from 1–800th to 1–1000th of an inch, make their appearance. In some there are at intervals divisions. The chemical composition appears from microscopic reactions to be of an albuminous nature. By the fourth day they are fewer and larger, and in the later stages they are no longer seen. If the local affection is at all severe, blood-cells, and occasionally a considerable quantity of blood, may be found in such milk.

Mammitis.—This disease, as its name implies, signifies an acute inflammation of the mammæ. Theoretically, milk secreted by an inflamed organ should be altered much in quality; but, in the case of a heifer suffering from this disease, milk taken the second day after calving did not appear to differ essentially, either in microscopical appearances or in chemical composition, from normal milk. Its specific gravity was 1·0362, and the composition of the solids in 100 parts was as follows:—

Milk-fat,	2·800
Caseine,	4·025
Albumen,	·560
Milk-sugar,	5·541
Nitrate of mercury precipitate dried at 100°,	1·68
Ash,	·920
Chloride of sodium in ash,	·110

Parturient Apoplexy.—A Cow suffering from Parturient Apoplexy; Pulse Imperceptible; Temperature 99°·4. Third day after Calving.

Specific gravity, 1·037. Reaction feebly alkaline.

	In 100 cc.
Milk-fat,	3·750
Caseine,	4·025
Albumen,	1·145
(Weight of mercury precipitate,	1·38)*
Ash,	0·980
NaCl in ash,	0·102

Urea was absent; there was much lactochrome. No abnormal elements detected by a microscopical examination.

* At the time of the analysis the compound nature of the mercury precipitate was not known.

The Milk of a Cow suffering from Pneumonia fourteen days after Calving. Pulse 82, *Temperature* 102°·4.

Specific gravity, 1·0297.

	In 100 cc.
Milk-fat,	2·965
Cholesterine,	0·580
Caseine,	3·860
Milk-sugar,	3·880
Albumen,	0·430
Galactine,	0·090
Urea,	0·005
Ash,	0·800
NaCl in ash,	0·488

This is the only milk in which the writer found an estimable quantity of cholesterine. The microscopical results were negative.

Engorgement of Rumen and Congested Liver. Pulse 68, *Temperature* 101°.

Specific gravity, 1·032.

	In 100 parts by weight.
Milk-fat,	6·057
Caseine,	4·796
Albumen,	1·067
Milk-sugar,	4·497
Galactine,	0·113
Ash,	0·670
NaCl in ash,	0·092

The milk appears simply concentrated.

Phthisis.—A Cow, five years old, with Extensive Tubercular Deposit in Right Lung. The Dam was also Scrofulous.

	Dec. 7, 1878.	Feb. 1879.
Specific gravity,	1·0297	1·0340
	In 100 cc.	In 100 cc.
Milk-fat,	2·77	3·83
Caseine,	3·650	5·4
Albumen,	0·867	0·365
Milk-sugar,	2·824	3·34
Galactine,	?	?*
Ash,	0·866	0·770
NaCl in ash,	0·096	0·15

A careful microscopical examination could detect no abnormal elements.

* The determinations of galactine were made on so small a quantity as not to be reliable, but this is certain that the galactine was beyond the average.

Phthisis.—A Cow, two years old, in an advanced stage of Phthisis.

	Jan. 29.	Feb. 17.
Specific gravity,	1·0329	1·0335
	In 100 cc.	In 100 cc.
Milk-fat,	2·599	3·280
Caseine,	3·000	3·980
Galactine,	?	0·250
Milk-sugar,	2·888	4·100
Ash,	0·910	0·780
NaCl in ash,	0·10	0·15

The entire amount the cow yielded in January was 1 gallon; the amount sent for analysis was a fractional part of the whole.

A Sample of Milk drawn from an Udder actually Infiltrated with Tubercular Deposit.

Specific gravity, 1·018.

	In 100 parts by weight.
Water,	94·640
Caseine,	1·210
Albumen,	2·387
Milk-sugar,	0·470
Milk-fat,	0·490
Alkaloids,	absent
Urea,	0·039
Ash,	0·764
NaCl in ash,	0·430
Nitric acid in combination,	0·018

The whole quantity of the fluid did not exceed 70 cc. It was of a dirty amber colour, with the caseine partially separating. A microscopical examination showed very few fat globules, and the following abnormal elements:—

1. Clusters of oval or round granular cells, for the most part ·0005 inch in diameter, with a well-marked oval nucleus.

2. Granular masses, irregular in shape, varying in size from about 0·0006 inch to ten or twelve times that size.

3. Granular rounded bodies, stained brilliantly by magenta or carmine.

This, then, is phthisical milk in its most intense form, and one never likely to be found in commerce, but admixture of such a fluid with genuine milk is possible.

It is essentially an albuminous serum, containing urea, small quantities of nitrates, common salt, and just sufficient caseine and milk-sugar to show its origin from a much diseased milk-gland. The absence of galactine is noteworthy.

Local Affection of the Udder.—Milk from a Heifer two days after calving, suffering from Retention of Fœtal Membrane, a portion of the Udder much inflamed.

The milk was pink in colour, and contained about a twentieth of its bulk in blood; it was perfectly fresh when examined, but rapidly putrefied. The blood was separated by subsidence as much as possible. The reaction was feebly acid:—

Specific gravity 1·0313.

	In 100 c.c.
Milk-fat,	4·40
Caseine and milk-sugar,	9·81
Albumen,	0·62
Galactine,	0·269
Ash,	1·16

§ 156. *Typhus.*—The milk of cows suffering from typhus has been analysed by Husson,* who states that from the commencement of the malady, the azotised principles augment, and that there are often found bloody and purulent fluids admixed. The following is an average sample of milk from cows suffering from a not too severe form of typhus:—

Fat,	1·493
Milk-sugar,	3·140
Albumen,	2·060
Salts,	1·850

§ 157. *The Propagation of Disease through Milk.*—Modern researches on zymotic diseases have for long been converging to the one conclusion, that these diseases are all produced by germs, the life-history of which is analogous to that of bacteria; and that, consequently, such diseases are only special forms of fermentation or putrefaction in living tissues, the disease-zymads growing and multiplying at the expense of the tissues.

Now, if the composition of milk and of the tissues be compared, it will be seen that milk, although physically a fluid, yet resembles in its chemistry a tissue, and contains all that is necessary for the nourishment and growth of a zymad. Hence it is, that if a scarlet-fever zymad, or a typhoid zymad, fall into milk, for all practical purposes it is immersed in a tissue; and there are plausible grounds for believing that, if the conditions of the temperature are favourable, the *zymad* may increase and multiply in the fluid. However this may be, milk certainly possesses no destroying power over these disease-germs or zymads; and there

* *Comptes Rendus*, t. 73, 1871, p. 1339.

are on record a number of well-authenticated outbreaks of typhoid fever, of diphtheria, and of scarlet fever, in which no reasonable doubt exists as to the milk having played the part of an infected garment, and conveyed the disease. The exact way in which the poison gained access to the milk in these various cases has not always been clear; but we may presume that adulteration with specifically tainted water, the handling of dairy utensils by persons whose hands have been soiled with the discharges of the sick, the dropping of epithelial scales into the milk-cans in the course of transmission, are all possibilities, and all likely to have the effect of tainting the milk. It will be unnecessary to go further into this well-worn topic, full details of which are to be found in the annual reports of the Local Government Board and elsewhere. We therefore pass on to a subject upon which less is known, and upon which there may be considerable diversity of opinion—viz., the spread of consumption through milk.

The question as to whether this actually occurs or not, hinges upon another very debatable point, and one on which the leading pathologists are by no means agreed—viz., is tuberculosis infectious, or is it not? further, is it possible to propagate tubercle through specifically-infected food or drink, or is it not? If the possibility of transmission of tubercle by infected food is proved, then it is scarcely possible to deny that tuberculosis may be caused by specifically-tainted milk. Villenin * was one of the first to attempt to ascertain, by direct experiment, whether tubercle was transmissible or not. He inoculated the rabbit, the sheep, the dog, and the cat with human tuberculous matter, always in very small quantities, with more or less success. The experiments of Villenin were repeated, with infinite variation, by most of the leading pathologists of Europe; but their deductions were quite different from those of Villenin, for, on putting various substances (other than tuberculous matter) in the subcutaneous tissue of guinea-pigs, they produced a febrile disorder, and found after death products which, they declared, were not to be distinguished from tubercle. Hence, tuberculosis was considered for a long time (and, indeed, is by some persons still so considered) as due to a mechanical irritation, chiefly set up in the delicate cells lining the lymphatic channels. While animals alone were the subject of the French, German, and English experimenters, a doctor in Greece—Zallonis of Syra—actually inoculated the human subject—a man affected with gangrene of the foot—with tuberculous sputa. In thirty-eight days the man died with unmistakable tuberculous signs, which an autopsy con-

* "Cause et Nature de la Tuberculose."

firmed. The opinion* that the introduction into the tissues of a great variety of foreign matters will cause this malady is now losing ground, there having been of late years some most valuable experiments on the subject, more especially those by Bollinger and by Cohnheim.†

The most striking of Cohnheim's experiments were those in which he introduced tuberculous matter into the anterior chamber of the eyes of kittens; the animals generally became infected after a well-marked period of incubation of from fourteen to twenty-one days. Cohnheim, associated with Solomons, has also proved the possibility of aerial infection, having produced the disease in animals by causing them to inhale tuberculous dust. The pathological changes thus produced they compared side by side with those produced by mere irritants, whether breathed or introduced into the system by other channels; and they declare, as the result of such comparison, that the products of the latter are entirely different, and not to be confounded with tubercle. Direct experiments with the milk from tubercular cows have been made by Gerlach, Klebs, and Bollinger. Gerlach fed two calves, two pigs, one sheep, and two rabbits for three weeks with the unboiled milk of a phthisical cow; the whole of the animals became affected with tubercular disease. Klebs made a similar successful experiment with nine guinea-pigs. The accidental infection of a large St. Bernard dog, which, having come across the milk designed for one of the experiments, drank it, and became tuberculous, is perhaps more striking than a formal experiment. The experiments of Bollinger were on pigs, as follows:—Two young pigs were fed with the unboiled milk of a cow which in life exhibited symptoms of lung disease, and which a *post-mortem* examination showed to have suffered from phthisis. This experiment was negative. The pigs enjoyed good health, and on being killed proved to have all their organs in a sound condition, with the single exception of some slight infiltration of the glands of the neck in the case of one. In a second experiment, the milk of a highly tuberculous cow was given for ten weeks to four healthy young pigs three weeks old. During this time a general enlargement of the lymphatic glands of the neck was observed; at the end of four and five months the animals were killed, when tubercular infiltration of the lungs, liver, spleen, &c., was fully established. Another experiment was made on a young pig, fed with the same milk for fourteen days. On killing the animal three weeks after-

* "The Transmissibility of Tuberculosis," by G. Fleming, *Med. Chir. Review*, Oct., 1874.

† "Die Tuberculosen vom Standpunkte der Infectionslehre," von J. Cohnheim. Leipzig, 1880.

wards, there was found cheesy inflammation of the large intestine, an exquisite miliary infiltration of the lungs, and a slight cheesy deposit in the bronchial glands. The milk in all the above experiments had been given unboiled. In another experiment, however, in which six pigs were taken, four were fed with the milk of the same cow (two with the unboiled milk, two with the boiled milk), and two were fed on ordinary diet to control the experiment. After a few months the last two were healthy; the two fed on unboiled milk highly tuberculous; one of the pigs fed on the boiled milk, on being killed, was found perfectly healthy; the other, killed a little later, was tuberculous. Further experiments are in progress.*

On the other side, there are numerous failures, and many observers have failed to propagate the disease. E. Perroncito, of Turin, records the case of a whole family (consisting of a man, his wife, and two children) drinking for eight days the milk of a cow most decidedly tuberculous, as proved by an autopsy; and yet they remained well. Negative results are, however, of little value, unless extremely numerous. If the disease can be propagated by milk, it does not necessarily follow that every animal experimented upon will become infected; for there are numbers of facts proving that some human beings and some animals have a great resisting power, and do not, with any readiness, take such diseases. It has hitherto been almost universally taught, that bovine tuberculosis has nothing essentially different in its course or pathology from human tuberculosis. This view has, however, been recently contested, Dr. Charles Creighton, in a very able paper,† giving a series of cases (eight in number) in which he contends that there was more analogy to "*Perlsucht*, bovine tuberculosis," than to human, and moreover, that this form is a distinct form, quite as distinct as glanders—the salient points in the cases cited being, (1.) the occurrence of tumour-like embolic infarcts in the lungs; (2.) the implication of the bronchial, or of the mesenteric and portal lymphatic glands; (3.) the characters of the eruption in the serous membranes, and its relative frequency; (4.) the microscopic appearances; (5.) the elements of obscurity in the cases viewed as cases of ordinary or autochthonous tuberculosis.

The very important information as to what percentage of cows suffers from the disease, and whether it is on the increase or decrease, is unfortunately not with any accuracy known; and from the contradictory statements advanced, all that one can

* *Aerztlich. Intelligenz Blatt*, No. 47, 507.

† An Infective Variety of Tuberculosis in Man, identical with Bovine Tuberculosis, Perlsucht, by C. Creighton, M.D., *Lancet*, June 19, 1880.

gather is, that it is rare in some parts, frequent in others, and that milch cows are especially prone to the disease.

Cruzel affirmed that in France, in every hundred old oxen fattened and slaughtered for food, one-half would have the lungs more or less tuberculous. Not very long ago, however, M. Vallin, aided by some of the most eminent veterinaries in Paris, searched for four months in vain for a tuberculous cow, and he states* that, out of 28,000 beasts slaughtered annually at the abbatoirs, only 20 to 28 bore any sign of tubercle, while those rejected as unfit for slaughtering are an insignificant number. On the other hand, in Germany the percentage of cows affected is about 2 per cent. In England the number is not known, but it certainly is not higher than 2 per cent., and it is doubtful whether it ever attains, except in certain localities, 1 per cent. The analyses of the author have shown that in the milk in the last stages of disease only (in the stages, indeed, in which it would be unprofitable to milk a cow), does the fluid essentially differ from normal milk; and the very milk so successfully experimented with by Bollinger was also found, on analysis, to be of normal composition. Hence, the danger is not imaginary, but real; and when we consider the enormous scale on which some dairies are conducted—the number of gallons of milk from various cows, which are mixed together—it is certain that, in large towns, specifically-tainted milk is constantly drunk. A great portion of such milk is raised before use to nearly the boiling point, but much is drunk unboiled.

Aphthous Fever.—The physical and chemical characters of aphthous milk have already been described. In certain stages of the disease, the milk acts upon young calves like a virulent poison, the calf dying from apnœa with great suddenness. After death few marked changes are noticed, save intense pulmonary congestion, and a somewhat injected patchy tongue. The milk has been given to pigs with a fatal result, and even cats have suffered indisposition from it; nor is there wanting the strongest evidence to show that it may convey the aphthous disease to man. This transmission to man has been observed for some time, for in the middle of the eighteenth century Michael Sagar† described the aphthous epidemic, which prevailed in Moravia, 1763-64, and related how the milk propagated the disease to animals and men. In 1834 three German veterinarians‡ (Hertzwig, Mann, and Villain) made on themselves some very conclusive experiments,

* M. Vallin, Lait des Vaches Phthisiques. *Annales D'Hygiène Publique*, July, 1878.

† *Libellus de Aphthis Pecoris*, Vienna, 1765.

‡ "Nouveau Dictionnaire de Médicine Véterinaire."

each taking a pint of the warm milk drawn from an infected cow for four consecutive mornings. On the third day M. Hertwig had feverish symptoms; by the sixth, the mucous membrane of the mouth was swollen; by the seventh, there was a well-marked eruption on the edge of the tongue, the lips, and the internal surface of the cheeks; by the tenth, the vesicles continually increasing in size, had burst; and by the twenty-fourth day the ulcers had dried, and there was some desquamation. MM. Mann and Villain were also affected in the same way, but to a less degree. This experiment is supported by a number of instances of partial epidemics in the human kind, which could be satisfactorily traced to aphthous milk. It would appear certain, that such milk after boiling is harmless. For example, Boulay records that foot-and-mouth disease, when imported into the Commune of Morchier by a pig-dealer, extended in a few days to over a hundred head of cattle, but spared the calves, which were fed on boiled milk and water, and not allowed to suck their mothers.

A New Form of Febrile Disease Associated with Milk.—The milk from a dairy near Aberdeen appears to have been the propagating agent of a peculiar and entirely new malady. This remarkable outbreak has been investigated and described with great ability by Dr. Ewart.* Twenty persons were attacked, and there were three deaths. The symptoms consisted essentially of fever, with one or more relapses, and swelling of the cervical glands, frequently ending in suppuration. The connection of the epidemic with the milk-supply was established by the fact of the illness being confined to those who drank the milk, as well as by the microscopical appearances of the milk, and some well-devised experiments on animals. The microscopic appearances of the milk showed:—

1. Numerous micrococci, some free others in groups or chains.
2. Numerous spores and cells of the yeast-plant.
3. Spores similar to *B. anthracis.*

Some pus from the neck of one of the patients was found to contain bacilli and spores apparently identical with those found in the milk, and such pus caused fatal illness when injected into small animals subcutaneously. These elements were submitted to cultivation, and a variety of experiments on rats were instituted with the suspected milk, side by side with control-experiments with healthy milk, the main result being to prove satisfactorily a direct connection between the bacilli and the

* On a New Form of Febrile Disease associated with the Presence of an Organism distributed with Milk from the Oldmill Reformatory School, Aberdeen, by J. Cossar Ewart, M.D., *Proc. Roy. Soc.*, 1881, xxxii., 492.

disease; the evidence pointed to a contamination of the water supplying the dairy, and the author concludes that the organism producing this new fever was morphologically not unlike the anthrax organism in its mode of development and life-history; and, further, that it was introduced into the milk after it had left the udder.

DECOMPOSITION OF MILK.

§ 157. It has already been stated that milk left to itself at all temperatures above 9° begins to evolve carbon dioxide, and that this is simply a sign and result of fermentation. If this fermentation is arrested or prevented by any of the means described in the section on the preservation of milk, the fluid remains perfectly sweet and good for an indefinite time.

Besides the production of carbon dioxide during decomposition, a certain portion of milk-sugar is converted into lactic acid, some of the caseine and albumen broken up into simpler constituents, and a small proportion of alcohol produced, which by oxidation appears as acetic acid, while the fat is in part separated into free fatty acids, which ultimately unite with the ammonia produced by the breaking up of the albuminoids. This fermentation of milk is a special kind which of late years has been much studied, and is known as *lactic fermentation*. Accompanying lactic fermentation, there is nearly always a weak butyric and a weak alcoholic fermentation.

The researches of Pasteur have established the fact that lactic fermentation is produced by a special organism as capable of being sown, cultivated, and, as it were, reaped, as a plant of higher and more complex character. This minute plant consists, like yeast, of a single cell, and propagates like yeast by rapid budding; in mass it is also similar in appearance to yeast, being viscid and of a gray colour. Under the microscope the cells are, however, seen to be very much smaller than those of the yeast-plant, and in common with all very minute particles to be agitated with a rapid "*brownian*" movement.

A small portion of this ferment, on being added to a solution of sugar, rapidly turns it acid; but the change to lactic acid is never complete, for acidity interferes much with its growth, and brings it ultimately to an end. If, however, the liquid is kept neutral by the addition of chalk, or by any other suitable means, under such conditions most of the sugar is converted into lactic acid. This change is very simple, being merely a splitting

up of one molecule into two more simple equivalent ones, thus—$C_6H_{12}O_6 = 2\ C_3H_6O_3$.

In a few rare instances, butyric fermentation and putrefaction take, in some degree, the place of lactic, and the milk becomes horribly offensive; but this is unusual, and, for the most part, even when the milk is much decomposed, a peculiar, sour, rather faint odour only is noticed. Nevertheless, a *weak* butyric fermentation is generally present with the lactic; the chief reason why it rarely proceeds to any extent being the fact that an acid medium is very unfavourable to the growth of this particular ferment.

According to Pasteur, the butyric ferment is essentially an infusorium of the genus Vibrio. The little organisms constituting the ferment have the appearance of minute cylindrical rods, rounded at the extremities, usually straight, either isolated or united in a chain of two, three, or four joints, and even of more. The diameter of these small rods is generally $\frac{2}{1000}$ of a millimetre, and the length of the isolated portions from $\frac{2}{1000}$ to $\frac{20}{1000}$ mm. [·0000687 to ·000687 inch]. They move forward by sliding. During this movement their bodies remain rigid and undulate slightly; they spin round, they balance themselves on end, and agitate their extremities; they are often bent. The method of reproduction is by fission.* The most favourable conditions for its development are a suitable liquid, slightly alkaline or neutral, kept at a temperature of 40°; the ferment does not require free oxygen.

§ 158. *Blue Milk.*—Milk has, in rare instances, been known to undergo a peculiar change of colour, becoming of a very marked blue tint, the seat of which is said to be the caseine. On adding caustic alkalies, the colour changes to a cherry red, but the blue is restored by acids. This change is without doubt due to a fungoid growth; the blue principle has never been isolated, but it appears to be volatile.†

ADULTERATION OF MILK.

§ 159. The adulterations of milk in this country, taken in the order of their frequency, are:—The addition of water, the

* M. Pasteur, *Compt. Rend.*, 52, p. 344, February, 1861.

† On blue milk, the following may be quoted:—Fuchs: *Magasin für die Gesammte Thierheilkunde*, 7, 133 to 198. Ehrenberg: *Monatsberichte der Berliner Akademie des Jahres*, 1840, p. 202. Erdmann: Bildung von Anilinfarben aus Proteinkörpern. *Journ. für Prak. Chemie*, vol. 99, 404, 1868. Haubener: *Magasin für die Gesammte Thierheilkunde*, Bd. 18, p. 1 to 85; 129 to 204, 370 to 282.

abstraction of cream (or both combined); the addition of cane sugar to conceal watering, the addition of salt, borax, or salicylic acid to milks likely to decompose; and, lastly, the addition of glycerine. Milk is also occasionally manufactured from condensed or concentrated milks. No other adulterations than the above* have been proved to exist by any trustworthy evidence. The mere addition of water is easily detected by the low specific gravity of the milk, which test is really extremely satisfactory, provided the milk is not exceptionally rich in cream, for an exceptionally rich milk may possess a specific gravity similar to that of a watered milk. For instance, a sample of "fear milk,"† analysed by the author, was found of a specific gravity of 1·019; it contained over 7 per cent. of milk-fat. If, however, the milk is allowed to stand a little while, and the fat then partially removed by skimming, a mistake from specific gravity is not possible. The specific gravity may be taken by the hydrometer, by a Westphall's balance, by a spiral balance (p. 70), or by a specific gravity bottle; in all cases it must be considered as a preliminary test only, its indications should be confirmed or otherwise by subsequent analysis. The *amount* of water in the milk can only be discovered accurately by analysis and calculation. The analysis is conducted on the principles already explained, and the amount of water calculated from the percentage of "solids not fat." If the exact composition of the

* The fable of the adulteration of milk with brains probably originated in a communication made to the *Gazette des Hopitaux*, Sep. 25, 1841, by an anonymous writer, who affirmed that he had seen in milk, by the aid of the microscope, cerebral tissue and the *débris* of blood-vessels. This improbable announcement was reiterated by M. Jules Rossignon, who, writing in *L'Echo du Monde Savant*, gave as an established fact the brain adulteration of milk ("La Cervelle des Chevaux de Montfaucon"). This statement again having been reproduced in *Le Memorial Encyclopédique*, was afterwards worked up, with additions and amplifications, in various popular periodicals and journals; but, generally speaking, it was not accepted by chemists actually engaged in practical work. In 1844, shortly after the publication of the papers alluded to, MM. Garnier and Harel declared in their work ("Des Falsifications des Substances Alimentaires"), "We have never met in commerce a single sample of milk falsified with brain; we have examined milk bought in different quarters of Paris, and especially among the poor, but we have never found an atom of cerebral matter." With regard to cream also, they justly say, that brains are not suitable for the production of cream, communicating to it a disagreeable taste, and not thickening it. Gautier de Chaubry also undertook some elaborate experiments, showing how extremely difficult it was to mix brain-matter with milk, and when it was effected, how different the milk was from ordinary milk.

† A small can of exceptionally rich milk has been occasionally carried by milkmen for the purpose of serving any inspector. Such milk has been termed "fear milk."

original milk is known, then the amount of water added may be with accuracy calculated from the following formula:—

$$\frac{100}{y} s = x$$

in which y denotes the original amount of "solids not fat," s the amount of "solids not fat" in the watered sample, and x the number of parts of genuine milk in 100. As this useful knowledge is in practice never obtained, the analyst must use a formula based either on the average percentage of "solids not fat," or on the lowest percentage known to occur. This average thousands of analyses have determined to lie between 9·3 and 9·5 per cent., while the lowest percentage found in healthy fairly-milked animals is about 9 per cent. Calculated on this basis, the formula becomes

$$\frac{100}{9} s = x$$

This is the standard adopted by the Society of Public Analysts; but as a standard it is too low, and permits the milkman to water the milk at least 2 per cent.; for instance, in the analysis of the milk of 183 cows, milked in the presence of Mr. Carter Bell, and analysed by him, the lowest percentage of "solids not fat" is given as 9·2. Now, to this milk water could be added in the proportion of 2½ per cent.; and as six of Mr. Bell's cows averaged "solids not fat" 11·3 per cent., such milk could be watered 25·5 per cent. Lastly, Mr. Wanklyn's average country milk could be watered 4 per cent.; his average town milk 10 per cent.; the milk of the Alderney cow 4 per cent.; and Mr. Bell's mean of 181 cows (9·9) 9 per cent., to bring it down to the Society's standard.

The author has, therefore, somewhat departed from standards in certifying to the adulteration of milk by water; and in cases where the "solids not fat" exactly reach the Society's standard, invariably analyses the milk carefully, seeking for evidences of watering in the presence of nitrates and sulphates. For cows' milk only contains a trace of sulphuric acid in combination, and is absolutely destitute of nitrates; water, on the other hand, not unfrequently abounds in sulphates, and, if impure, in nitrates. Hence, if a sufficient quantity of the milk can be obtained for the investigation, the finding of nitrates and an excess of sulphates, or both, is fair proof of watering, and an analyst is justified in certifying accordingly, although "the solids not fat" may reach the so-called standard.* In certify-

* This is the more necessary since, at the present time, the Government chemists have adopted the untenable standard of 8·5 "solids not fat."

ing as to watered milks, the author, in certain cases, uses in his certificate a particular form of words, which is calculated to represent the actual facts more accurately than the usual statement. An example will suffice :—

"*This milk has been adulterated with water. The exact amount of water added can only be told when the original composition of this particular sample of milk is known. But if the original milk was a very rich milk, containing* 11 *per cent. of 'solids not fat,' then to every* 100 *parts of milk by weight* 22·7 *of water have been added.** *If the milk contained* 10 *per cent. of 'solids not fat,' then* 15 *parts of water to every* 100 *of milk have been added. Lastly, if the composition of the original milk was that of the poorest milk which a healthy, fairly-milked cow is known to yield as an average—viz., containing* 9 *per cent. of 'solids not fat,' then to every* 100 *parts of such milk* 5·6 *of water have been added; or, to put it in another form,* 1000 *parts by weight of milk have been made into* 1056. *I therefore certify the milk to have been watered AT LEAST* 5·6 *per cent.*"

However verbose such a certificate may seem, yet when it is remembered that under the Act the analyst is seldom called upon to give verbal evidence before a magistrate, the more full and complete the written statement of facts the better, and the author has occasionally found it in practice extremely useful, more especially since few magistrates possess chemical knowledge, and, therefore, naturally expect and require a very full explanation of the principles on which the certificate is based.

§ 160. With regard to the removal of cream, the method of detection is, of course, to make a quantitative analysis of the milk, exhausting the dry solids, as before described, by suitable solvents. If the milk-fat so obtained falls below 2·5 per cent., the milk in all probability has had its cream removed; and the amount of fat abstracted is found, according to this standard, by the following formula, in which s = solids not fat, f = the fat found, and x the percentage of fat removed :—

$$\frac{2{\cdot}5}{9{\cdot}0}s - f = x$$

If the milk is both skimmed and watered, the following formula may be used, the letters having the same significance, with the exception that x means extraneous water :—

$$100 - \frac{100 + 2{\cdot}5}{9}s - f = x$$

* Possibly one cow in a thousand, at one period of the year, and on a particular diet, may give such a milk.

In giving a certificate as to the skimming of milk, the author invariably states that it is calculated to a particular standard, which may not at all represent the actual amount of fat removed, for in rich milks the fat is considerably over 2·5 per cent.; and he is also careful never to use the word "skimming," but substitutes the phrase "the fat has been abstracted," a formula which includes all the indirect ways in which fat may be removed.

The "solids not fat" may be normal, and the specific gravity normal, and yet the milk may be much watered. This feat is accomplished by the addition of cane-sugar. Cane-sugar is cheap, its solution in water has a high specific gravity, and it, of course, raises the amount of "solids not fat." A little practice in tasting milk enables any one to suspect its presence, but a complete analysis alone establishes it. In a milk adulterated in this way with cane-sugar, if the milk-fat, the caseine, and albumen are separately estimated, the caseine, albumen, and probably the milk-fat will all be found low, while the ash will also be found less than the normal quantity, and the remaining organic constituents high.

Dr. Muter estimates the amount of cane-sugar added, by pouring 10 grms. of milk on to 4 of calcium sulphate hydrate, evaporating this mixture to dryness with constant stirring, exhausting the fat by ether, and then removing all the sugar by dilute alcohol. This alcoholic extract is made up to a known bulk, and divided into two parts; one portion is evaporated to dryness, weighed, and then burnt, and the weight of organic constituents found by difference; in the other portion an estimation by Fehling is made; if no cane-sugar is present, the difference between the two estimations will be merely due to galactine and other principles soluble, to some extent, in dilute alcohol, and to any experimental error. If, however, cane-sugar has been fraudulently added, there will be a most marked difference, which may be returned as cane-sugar. Dr. Muter considers that unless the sugar is sufficient to impart a taste to the milk, it is not likely to be with any certainty discovered by analysis.*

§ 161. The addition of common salt, carbonate of soda, or, speaking generally, mineral adulterants, if in large quantity, will be at once recognised by the abnormal weight of the ash. If in smaller, the relation existing between the amount of ash and the caseine will be destroyed, and render it necessary to submit the ash to a careful qualitative and quantitative analysis.

* *Analyst*, March, 1880.

A normal milk-ash is white, or nearly so, contains scarcely a trace of sulphate, and does not effervesce on the addition of acids. Borax is difficult of detection, because so little is usually added. The best method would appear to be, to evaporate down as much of the milk as can be obtained, previously rendering it feebly alkaline. It is then burnt up at a low temperature to an ash, and a little glycerine added; the mixture stirred with a glass rod, and a portion on the loop of a platinum wire introduced into the Bunsen flame, and examined by the spectroscope, when the bands peculiar to boracic acid will be seen, and may be compared with the spectrum of pure boracic acid. Or the ash may be decomposed by pure sulphuric acid, the freed boric acid dissolved out by alcohol, the alcohol concentrated, and the platinum wire moistened as before, and the spectrum observed. The flame in all these cases will show a more or less marked green colour.

A process of preserving milk by glycerine exists, and occasionally it is found in milk. To detect glycerine the caseine, fat, and albumen must be separated by dilution, acetic acid, carbon dioxide, and heat, as described at p. 241. The sugar is then estimated in one portion of the yellow whey by copper solution; the remainder is first neutralised, and then evaporated to dryness, and freed from any trace of fat by exhaustion with pure ether. The glycerine is now dissolved out by a mixture of alcohol and ether, the alcohol-ether evaporated off, and the glycerine identified by its physical characters and the production of acrolein fumes when heated with sulphuric acid. Use may also be made of the fact that glycerine sets free boracic acid from borax. A little borax, therefore, may be moistened with the syrupy drops supposed to be glycerine, heated in a Bunsen flame, and examined before the spectroscope for the boracic acid bands.*

Salicylic acid is used occasionally as a preservative of milk, and it is easily detected by shaking up milk whey (first acidified by hydrochloric acid) with ether. The ethereal solution on evaporation leaves the acid in a pure enough state to permit the successful application of reagents. The best test for salicylic acid is the beautiful violet colour which it gives with a neutral solution of ferric chloride. Besides this test, a minute portion may be placed in the subliming cell, when a well-marked sublimate is obtained at about 100°. The crystalline form of this sublimate may be compared with one obtained from a known pure sample of salicylic acid.

* A. Senier and A. J. G. Lowe: *Chem. Soc. Journal*, clxxxix., Sept., 1878.

PRESERVATION OF MILK.

§ 162. It has already been stated that the lactic fermentation and the putrid, or butyric, fermentation of milk are both due to mysteriously minute bacteroid bodies, ever present in the atmosphere.

Milk boiled, or raised to a sufficiently high temperature to destroy any germs which may be already in the milk, and then kept by any process whatsoever in such a manner that germs cannot gain access to it, remains sweet for an indefinite time. If, for example, a flask of milk is taken, heated up to its boiling-point for some time, and then, *while boiling*, plugged in the neck with a good compact piece of fibrous asbestos, which itself has been made for a few minutes red hot, the milk will neither decompose nor ferment. Similarly, with suitable precautions, the long thin neck of a flask may be bent in an N shape, the milk boiled as before, and allowed to cool; in this case, also, there will be no decomposition. The explanation in the one instance being that the germs have been filtered; in the other, that they have settled in the bend of the N, not being able to turn corners readily. Similar experiments (all of which have been essayed over and over again by Tyndall, Pasteur, and others) all point to the same simple conclusion—viz., that it is only necessary to destroy the existing germs, and then put the organic substances or fluids under such conditions as will shield them from renewed infection, in order to preserve the most complex substances and fluids from further change.

The various processes which have been proposed for the preservation of milk fall under the following heads:—

(1.) *Evaporating Processes,*—in which the milk is reduced to a dry powder, and generally mixed with sugar, the evaporation taking place either in a vacuum or in a stream of warm, dry air.

(2.) *Chemical Additions,*—such as glycerine, or other anti-ferments.

(3.) *Application of Cold.*

(4.) *Application first of Heat, and then of Cold.*

§ 163. (1.) *Evaporating Processes.*—All putrefactive and fermentative change is reduced to a minimum when organic substances are deprived of water, and milk is no exception to the rule. The dried milk solids, without any addition whatever, will often keep for many weeks although freely exposed to the air; while with certain additions, such as sugar, the preservation may be called for practical purposes permanent.

The Swiss Company's Condensed Milk may be cited as a very successful experiment of this kind, the milk being what it pre-

tends to be—viz., evaporated to a certain point with the addition of sugar. Numerous patents have also been taken out in this country with the same end in view. A few of the more important are as follows :—

In William Newton's patent [No. 6787, 1837] the milk was evaporated as rapidly as possible, either by warm or cold air or in a vacuum, and then pulverised and mixed with powdered loaf-sugar.

In 1847, a process was proposed by T. S. Grimwade [patent No. 11703]. The milk was concentrated *in vacuo*, and four grains of saltpetre were added to every quart; the milk was then transferred into vacuous bottles, the arrangement for corking these bottles being particularly ingenious.

Jules Jean Baptiste Martin de Lignac [patent No. 11892, 1847] evaporated in simple open pans, continually breaking the scum up by mechanical means. A little sugar was added, and the product preserved in hermetically-closed vessels.

A patent taken out by Grimwade in 1855 [patent No. 2430], was a combined process. The milk, immediately on being received from the cow, was heated to 110° Fahr.; and 5 ozs. of refined sugar and 1·25 ozs. of milk-sugar were added to every gallon of milk. The whole was now evaporated in a particular pan with double bottom, through which hot water was made to circulate during the evaporation. These pans were kept in a continual oscillation by means of machinery, and the resulting dry solids were ground to powder by rollers.

In Clark's patent [No. 3675, 1837], for the first time, is mentioned the heating of milk to the boiling point of water, with the avowed object of destroying germs. The milk is evaporated in a vacuum without the addition of sugar.

Stephens has an ingenious specification [No. 1342, 1872], according to which the milk is rapidly condensed in a continuous manner by successively passing through a series of twenty-four pans, each pan being raised a little above the next in order, and the whole being in a line. The bottoms of the pans are serrated, heated by steam, and oscillation by machinery is kept up. The milk flows in a slow shallow stream, and the evaporation is finished by the time the milk reaches the last pan.

§ 164. (2.) *Additions to Milk.*—The ordinary additions have been sugar, milk-sugar, glucose,* carbonate of soda, and nitre. Bethall, in 1848, preserved cream and milk by first expelling the air, and then saturating the liquids by carbonic dioxide. The gas was evolved in the usual way, from sodic carbonate

* J. A. Newnham, No. 2801, 1870.

decomposed by an acid; the air was expelled by boiling, and the milk was then preserved in bottles. A similar patent [No. 25, 1879] has been taken out by Riddell, and, without doubt, this method is scientifically correct, and, if properly done, would be effectual. Wanklyn and Eassie [patent No. 1861, 1871] have proposed the addition of two parts of glycerine to every 100 of milk.

All these methods of preserving milk have, it is obvious, no effect in destroying the germs of any disease possible to be communicated to man. Speaking generally, indeed, all additions to milk in the form of antiseptics, such as glycerine, salicylic acid, borax, and the like, should be looked upon with disfavour; for by their use cleanliness in the dairy would not be such an essential as it is now; and the addition of these antiseptics is somewhat analogous to the saturation of foul places with carbolic acid, when the more obvious and more effectual remedy would be to keep them free from filth.

§ 165. (3.) *Action of Cold on Milk.*—The simple action of cold on milk has been studied scientifically, and it has been conclusively proved that the artificial cooling of milk by ice (whether the milk be placed for the purpose in deep cans or in shallow pans) produces far better, sweeter cream than any other system. An analysis of cream by Voelcker * thrown up by the Swartz system,† gave the following:—

Milk fat,	85·70
Caseine,	·92
Ash,	·12
Water,	13·26

The cream was perfectly neutral.

Tisseraud,‡ from his experiments on the action of cold, concluded that—

1. The rising of the cream is the more rapid the nearer zero the milk is kept;
2. The volume of the cream is greater;
3. The yield of butter more considerable;
4. The skim-milk, the butter, and the cheese, are in the latter case of better quality.

Still, however valuable the use of cold may be to throw up the cream and to preserve milk in transit, it must not be forgotten that it in no way renders the milk safe, should it be contaminated by any specific poison of animal or human origin.

* *Journal Agricul. Soc.*, No. xxiv., 1879, p. 157.

† Deep cans, (2 feet long, 20 deep, and 6 wide), in which the milk is artificially cooled, are the chief features of the Swartz system.

‡ *Comptes Rendus*, t. 82, 1876.

§ 166. (4.) *Heating and then Cooling.*—A very perfect process of preserving milk, if the temperature used had only been sufficient, was patented in 1857, by Joseph House, No. 15. He evaporated down to ⅜ of its bulk, at a temperature not exceeding 150° Fahr., in a shallow circular dish. The concentrated milk was then put into tins, cooled artificially and soldered down.

INFLUENCE OF FOOD ON THE QUALITY AND QUANTITY OF MILK.

§ 167. The influence of food on the lacteal secretion is great, a difference more especially appreciated if the produce of the whole milk be taken into account, and not the mere percentage composition. Indeed, in experiments on the influence of food, the mere composition of 100 parts of milk, without the knowledge of the total amount secreted, is not only useless, but misleading, and has caused many erroneous conclusions.

It appears established that abundance of suitable food, with little exercise, increases the yield of milk in every animal, and therefore increases all the constituents; while the reverse decreases the yield, and therefore decreases all the constituents. The increase of the total solids, when a highly nitrogenous substance like flesh is given to a herbivorous animal, is remarkable. Thus, Weiske obtained daily 739 grms. of milk from a goat fed on potatoes and straw, but on the addition of a little powdered fibrine to the same weight of food, 1054 grms.

Dumas considered it proved by his experiments* that, when bread was given to a bitch, her milk then contained milk-sugar, but when carbo-hydrates or starchy substances were withheld, and flesh given, then there was no milk-sugar, and that in all the carnivora lactic acid took the place of lactose (milk-sugar). It would, however, appear that this teaching is erroneous; for most certainly the milk of animals fed exclusively on flesh, does contain milk-sugar, and it is probably of albuminous origin.

Beusch† has found milk-sugar in the milk of a bitch, the sample being drawn on the eighth, twelfth, and twentieth days of an exclusive flesh diet. Subbotin ‡ found the sugar in a bitch's milk to be 3·41 per cent. when fed on potatoes, and 2·49 when fed on meat; but since on the latter diet there was a far greater yield than on the former, the real fact was that the flesh increased, not diminished, the sugar.

* *Comptes Rendus*, t. xvii., p. 585, 1843.
† Beusch: *Ann. der Chemie u. Pharmacie*, lxi., s. 221, 1874.
‡ Subbotin: *Arch. für Path. Anatom.*, xxxvi., s. 561, 1866.

The connection of fat with the food eaten by the cow formed the subject of an interesting controversy between Liebig and the French chemists. MM. Dumas, Boussingault,* and Payen made several experiments on seven cows. These cows furnished annually 17576 litres of milk, specific gravity 1035; the weight, therefore, of the milk was about 18191 kilos., and the fat produced was 3·7 per cent., or 673 kilos. annually. The food supplied to the animals was 38325 kilos. of hay, and the fat contained in the food the authors calculated not to exceed 766 kilos., and then proceeded to draw the conclusion, that this milk-fat was derived solely from fat in the food eaten. Liebig replied to their paper, and showed that a cow nourished with 15 kilos. of potatoes and 7·5 of hay, received in six days 756 grms. of fatty matter; but the excrements furnished 747·56 grms. of fat, and the cow yielded 3116 grms. of butter. Hence the supposition was impossible.†

Kuhne fed cows on fat-rich and fat-poor foods for some time with entirely negative results.

We have also the extremely valuable experiments undertaken some years ago by Dr. Lyon Playfair, in which the food given to the cow was carefully weighed, and the milk produced was also weighed and analysed. The experiment lasted five days, and the following is a summary of the results:—On the second day, the cow received food which contained ·486 lb. fat, but the butter produced was ·969 lb., so that ·483 lb. (even supposing the fat taken in with the food to have been elaborated into butter) must have been derived from other sources. On the third day the cow received—

23 lbs. hay	=	·426 fat.
2·5 lbs. oatmeal	=	·050 ,,
8 lbs. of beans	=	·066 ,,
Total, . .		·542 fat.

But the butter amounted to ·9 lb., much in excess of the fat taken in. On the fourth day, the butter amounted to 1·36 lb., the fat in the food to ·364 lb. On the fifth day, the butter was 1·203 lb., the fat in the food ·29 lb. The total result being that the cow received 1·682 lb. fat in its food, and yielded 4·429 lbs. fat in its milk, giving 2·747 lbs. in excess of that received.

Weiske fed a goat as follows:—During the first period, it had 1500 grms. of potatoes and 375 grms. of chopped straw, when the

* "Recherches sur l'Engraissement des Bestiaux et la Formation du Lait," par MM. Dumas, Boussingault, et Payen: *Comptes Rendus*, t. xvi., p. 345, 1843.

† *Ibid.*, t. xvi., p. 553.

yield of milk daily was 739 grms.: of fat, 19·96 grms.: in the next period (25 grms. of flesh-meat were added); this brought the milk up to 1054 grms., and the daily yield of fat to 33·21 grms. Instead of the flesh-meat, 250 grms. of bran and 125 grms. of oil were next added; but this decreased the yield of milk to half the former quantity—viz., 588 grms., the fat being 29·74 grms. Instead of the oil, 85 grms. of stearic acid was added; the milk diminished slightly in quantity, 506·2 grms. of milk being obtained, and 22·30 fat.

The most extended series of experiments on the influence of food on the fat of milk and on the total yield are, however, those of Fleischmann and P. Vieth. They observed and registered the daily yield of milk, the percentage of fat, the specific gravity, and the difference between the morning and evening milkings under different diets in a herd of 119 cows. The observations continued a whole year.

The herd was of the dun-red Mecklenburg breed. Their average weight during the stall-feeding season being 453·5 kilos. (999·7 lbs.). Their dry period averaged, for each cow, fifty-five days, and the yield of milk of the whole herd was 2582·34 kilos. (5692 lbs.) each, or, expressed in gallons, 550 gallons. During the first period, from January 1 to March 5, their food consisted of 12 kilos. (26·4 lbs.) of chopped fodder—viz., one-fifth clover hay, one-fifth meadow hay, three-fifths oat and barley straw, together with ·875 kilo. (1·92 lbs.) long oaten straw, 1 kilo. (2·2 lbs.) wheat bran, and 1 kilo. (2·2 lbs.) cocoa-nut cake. The same rations were continued to May 15, with the slight addition of 0·375 (3·2 lbs.) of flesh-meat. From October 15 to December 31, the rations consisted of 4·165 kilos. (9·1 lbs.) clover hay, 1·75 kilos. (3·85 lbs.) meadow hay, 5·985 kilos. (13·18 lbs.) oaten straw—all long, ·5 kilo. (1·10 lbs.) cocoa-nut cake, ·5 kilo. (1·10 lbs.) rye-meal. The main results of the experiments are tabulated on the next page (Table XVI).

It will be seen that the fat was considerably more during the 2nd and 3rd periods—viz., from March to July, when flesh meat was a constituent of the food; besides, those months were of a pleasant temperature, therefore moderate warmth and a nitrogenous diet contributed.

The numerous experiments quoted show very conclusively that the main fat-producing foods are to be found among those that are highly nitrogenised, and that the farmer who desires to increase his yield of cream must certainly choose the nitrogenised rather than the starchy or fatty foods. Stall-fed cattle, as a rule, give more fat than those that are not stall-fed, for a portion of the fat appears to be diverted to keep

TABLE XVI.

Periods.	Milk per Cow.		Fat per Cow.		Remarks.
	Morn.	Eve.	Morn.	Eve.	
	Lbs.	Lbs.	Lbs.	Lbs.	
I. Jan. 1 to March 5, 65 days, . .	7·70	7·28	·26	·25	Stall-feeding.
II. Mar. 5 to May 15, 70 days, . .	8·84	8·49	·28	·27	Addition of flesh-meat.
III. May 15 to July 15, 61 days, . .	9·43	9·68	·31	·30	Pasturage on commons.
IV. July 15 to Oct. 15, 92 days, . .	7·39	7·19	·24	·24	Pasturage on clover-grass.
V. Oct. 15 to Dec. 31, 77 days, . .	5·81	5·43	·20	·19	Stall-feeding.
Day's average, . .	15·630		·51		

TABLE XVII.

Duration of Experiment.	Average Weight per head.		Daily Average Yield.		Daily Produce in Butter from the 8 Cows.
	Superior.	Inferior.	Superior.	Inferior.	
I. Feb. 22, March 1, .	1065 1087	1039 1042	9·48	6·49	3·4
II. March 19, . .	1097	1072	10·23	6·71	3·8
III. March 27, . .	1118	1085	9·54	6·12	3·6
IV. April 5, . .	1112	1118	8·99	6·31	3·9
V. April 14, . .	1094	1086	8·33	6·09	2·9
VI. April 22, . .	1116	1098	7·45	5·72	2·7

Food.—I. 18 lbs. of brewers' grains, 36 lbs. mangolds, and 25 lbs. oat-straw.
II. 5·4 lbs. rape-cake, 36 lbs. mangolds, 25 lbs. oat-straw.
III. 4·5 lbs. rape-cake, 36 lbs. mangolds, 25 lbs. oat-straw.
IV. 18 lbs. brewers' grains, 36 lbs. mangolds, 25 lbs. oat-straw.
V. 18 lbs. brewers' grains, 45 lbs. mangolds, 25 lbs. oat-straw.
VI. 12 lbs. brewers' grains, 45 lbs. mangolds, 25 lbs. oat-straw.

up the heat of the body, therefore it is a matter of practical economy to keep cattle warm in the winter. Similarly, the yield of milk becomes less in quantity and poorer in quality, if cows are allowed in the summer to be teased by dogs or flies, or in anyway compelled to take much exercise.

Struckmann made some very valuable experiments in 1859 upon cows of good breed, "superior," and cows of an "inferior" breed. The method of feeding and the results are tabulated in annexed table (XVII).

The conclusions drawn are—

(1.) That most milk is produced by a diet of 5·4 lbs. rape cake, 36 lbs. mangolds, and 25 lbs. oat-straw.

(2.) That a reduction of 9-10ths lb. of rape-cake diminished the milk of the superior cows, the eight cows in the 3rd period yielding about a gallon less milk daily; hence, 1 lb. of oil-cake produced 1·2 lbs. of milk.

(3.) In the sixth series, the cows received 6 lbs. less brewers' grains, which diminished the produce to the extent of about 1-10th of a gallon; thus, 1 lb. of brewers' grains produced about a quarter of a pound of milk.

(4.) In the first and third series, very nearly equal quantities of milk were produced. In both sets the same quantity of mangold-wurzel and oat-straw were given; 18 lbs. of brewers' grains of the first series were replaced in the third by 4·5 lbs. rape-cake; hence, 1 lb. of rape-cake equals 4 lbs. of grains in milk-producing power. The authors noted that rape-cake produced milk richer in butter than that obtained from cows fed on brewers' grains; but the butter in the last case had a better flavour. It is curious to note that the superior breed was more affected by change in diet than the inferior:—In the first period, the four superior cows gained 100 lbs. in weight, and yielded 343 gallons of milk; the four inferior gained 304 lbs. and yielded 227·2 gallons of milk; or, to put it in another form, in thirty-six days the superior cows produced 115·8 gallons more milk, and gained 204 lbs. less live weight than the inferior; from this it would appear, that 5¼ lbs. of milk were replaced by 1 lb. of flesh.

§ 168. The colouring and the alkaloidal and active principles of plants impart their distinctive properties somewhat readily to milk. Thus it has long been noticed that browsing on certain plants affects the colour of milk: *Caltha palustris*, saffron, and rhubarb colour it yellow; rhubarb, opuntia, and *Rubia tinctorium*, red; *Myosotis palustris*, polygonum, and *Anchusa equisetum*, blue. Purgative vegetables, such as rhubarb, or even the juices of acid fruits, taken by a suckling woman almost invariably affect the infant. There are instances of milk becoming

poisonous from containing the active principles of plants. In June, 1875, an epidemic of diarrhœa occurred in the Rhone Gorge, and was traced to goats' milk, the goats having browsed in fields where the meadow saffron was growing. Professor Ralti isolated colchicine from the milk. Similar outbreaks, caused by the animals having fed on poisonous shrubs, have been recorded in the Western States of America and Australia. There is a supposition that the exposure of a cow to bad odours, or to putrid emanations, has an influence on the milk. Mr. Willard cites instances of cows yielding milk quite unfit for making cheese, in consequence of the animals having inhaled the putrid emanations of a dead and decomposing cow. Mr. A. H. Smee* has also stated that the milk of cows fed on sewage farms rapidly putrefies, but no details as to the manner in which the samples were collected are given, and the explanation may be that the putridity of the milk was not due to the grass eaten, but that the teats of the cow were fouled by decomposing substances, which would mix with the milk and infect it. A most notable example of this is related by X. A. Willard.†

In a large American cheese-factory much trouble was caused by decomposition of the milk. The cause of this was traced to one farm, and it was ultimately satisfactorily demonstrated that the animals every day walked through a putrid slough, the matter adhered to the teats, there dried, and particles fell into the milk, with the usual result, so that the possible want of cleanliness in some of the details of milking must always be borne in mind in such inquiries, and especially the probable presence of bacteria on the external skin of a cow exposed to putrid emanations. The subject is of great importance, and needs further inquiry. In any future experiments as to the influences of grass manured with sewage on cows' milk, the teats and udder should be washed with a solution of some disinfectant before commencing the milking, and more than ordinary care should be taken that the receptacles are in a cleanly state.

§ 169. Experiments have been made with the object of ascertaining whether metallic compounds would be excreted by milk. Arsenic passes readily enough in minute quantities, and the same may be said of lead and oxide of zinc. Antimony also, if administered, appears in the milk. The statements with regard to mercury are conflicting, but the balance of evidence leads, on the whole, to the conclusion that it is not excreted, even in minute quantities, by the mammary glands. Bismuth,

* "Milk in Health and Disease," by A. H. Smee. London, 1875.

† "American Milk Factories," by X. A. Willard, A.M., of Herkemer, New York. *Journ. Agric. Soc.*, viii. 1872.

when administered, was detected in milk by Marchand, Lewald, Chevallier, and Henry. Lewald gave 15 grms. of potassium iodide to a cow, and its presence for four days afterwards was detected in the milk; 21 grms. were then given, and the drug could be detected so long as seventy-two hours afterwards. On administering it again, it was found in the milk for eleven days.

THE QUANTITY OF MILK GIVEN BY THE COW, THE METHOD OF FEEDING, &c.

§ 170. The capacity for milk of the udder of the cow is usually estimated at about 3 litres [·66 of a gallon, or a little more than 5 pints]. The quantity of milk secreted is about three times this amount, but varying in individual cows, and depending on circumstances, such as the breed, the health, the size of the cow, the time after parturition, and the nature and quantity of the food given.

§ 171. The breeds in England most approved of are the Alderney, Ayrshire, Holderness, Kerry, and Suffolk. In Germany, the Swiss, Allgäuer, and Dutch cows appear to be the favourites. Some careful estimates of the amount yielded by different breeds of Continental cows have recently been published as follows:—

TABLE XVIII.—AVERAGE YIELD OF MILK.*

	Litres per year.	Gallons.	Average yield in gallons per day.
Ausbacher,	1284	283·07	·77
Mürzthaler,	1500	330·70	·90
Voigtlander,	1600	352·76	·95
Simmenthaler,	1690	372·59	1·01
Saxony,	2023	446·01	1·22
Walzthaler,	2272	500·90	1·36
Pinzgäuer,	2338	515·45	1·40
Swiss,	2625	578·70	1·60
Allgäuer-Montafaner,	2697	594·60	1·62
Allgäuer,	2710	597·47	1·62
Oldenburger,	2751	606·51	1·65
Dutch,	2906	640·68	1·74

* *Abl. Centr-Bl. f. Agric. Chemie*, 1877, 236.

These breeds, then, are not superior to our own. The favourite cow of the London dairymen appears to be the Yorkshire cow, essentially a shorthorn. The average yearly yield is from 600 to 700 gals., 15 of these cows giving about 10,000 gals. of milk yearly, or 1·7 gal. per day; individual cows, of course, occasionally exceed this. A cow has been known to give daily for some time as much as 5 gals. of milk.

The time elapsing before and after calving causes, as might be expected, considerable variation in the mammary secretion, the quantity augmenting during the first two or three weeks, and diminishing towards the end of the third or fourth month. Towards the seventh month the quantity sinks to one-half, and in the ninth and tenth months it is often reduced to three-quarters of the quantity secreted at first. On the approach of calving, the milk ceases altogether.

The age of the animal has some influence, very young cows secreting less than mature adult cows. It is also found that, *cæteris paribus*, the larger the cow the greater the yield of milk. Mr. Ockle of Frankenfeld took four Dutch milking cows, two weighed 2112 lbs., and two others only 1537 lbs.; he fed them on the same food, and submitted them to similar conditions for sixteen days. The results of this experiment are embodied in the following table*:—

No.	Weight at commencement of experiment. lbs.	Weight at end. lbs.	Green Lucerne consumed. lbs.	Produce of milk. lbs.
Two heavy cows, .	2112	2102	4921	68
Two light ,, .	1537	1537	3859	48

	Produce in milk per 100 lbs. Green Lucerne. Galls.	Pints.	Ozs.	Lucerne consumed per 100 lbs. live weight.
Two heavy cows, ...	1	3	16	14·6 lbs.
Two light ,, ...	1	11	16	16·0 lbs.

§ 172. The feeding of milking-cows varies somewhat according to local circumstances. In town dairies brewers' grains are much in use, and one to two bushels are given daily, besides mangolds, hay, and meal to each cow. A very common course of home-feeding is as follows:†—At 4 a.m. the cow receives two or three pecks of grass, immediately after being milked, then 4 to 5 lbs. of hay; at 9 a.m., from 20 to 25 lbs. of chopped mangolds, and another 3 to 4 lbs. of hay; at 1 p.m. there is a second milking; another similar feed follows, and she is given plenty of water. If

* On Milk, by Dr. A. Voelcker, *Journ. Agricult. Soc.*, xxiv., 1863.
† T. Carrington: *Journ. Agricult. Soc.*, xiv., 1878, p. 670.

oil-cake is used, 3 to 4 lbs. a day are given either with the mangolds, or in a gruel with the grains. In the country the chief dependence is placed on hay, mangolds, barley-meal and bean or Indian flour; in the summer, abundance of green food is given, such as clover, vetches, cabbage, &c.

CREAM.

§ 173. Milk on being allowed to rest for some time becomes covered with a yellow fatty layer, known as cream. In composition it fairly agrees with ordinary milk, save that it contains a large percentage of fat, and that there is also a somewhat relatively higher percentage of caseine and albumen. The albuminoids have a tendency to separate partially, and mechanically adhere to the fat; for example, the author found the average composition of Devon cream as follows:—

		Per cent.
Milk-fat,		65·011
Caseine,		3·530
Albumen,		·521
Galactine,		·050
Lactochrome,		Undetermined
Milk-sugar,		1·723
Water,		28·675
Ash,		·490
Chlorine in Ash,	·013	
Calcic Phosphate,	·373	

It will thus be seen that the milk has thrown up caseine with the fat, for if we allow that ordinary milk contains 86·87 of water and 3·98 per cent. of caseine, then the amount of caseine in the cream, if none were separated, would be—

$$\begin{array}{ccccccc} \text{Water.} & & \text{Caseine.} & & \text{Water.} & & \text{Caseine.} \\ 86{\cdot}87 & : & 3{\cdot}98 & : & 28{\cdot}675 & = & 1{\cdot}31 \end{array}$$

But the cream, instead of containing 1·31 per cent., actually contains 2·22 in excess of this quantity.

The amount of albumen strictly follows the caseine, for the ratio of caseine to albumen in milk being as 3·88 is to ·77, the theoretical yield of albumen in this particular case would be ·66, the amount actually found being about ·1 per cent. lower than this estimate.

If the composition of the Devon cream shows clearly that there is some considerable separation of the caseine, the milk-sugar follows very closely the proportions one would expect to find from the amount of water; for, taking the average of 4·0 of milk-sugar dissolved in 86·87 of water, we get in the present case—

Water.		Sugar.		Water.		Sugar.
86·87	:	4·0	:	28·7	=	1·3

which does not deviate very considerably from the numbers actually obtained—viz., 1·723.

Devon cream is of the consistence of a soft paste, and is covered with a skin-like layer of partially dried caseous and fatty matter. This cream is produced by keeping the milk in large pans, at a gentle heat, for many hours. The temperature is always far under boiling point, yet probably sufficiently high to arrest fermentation. This application of a moderate heat during a lengthened time causes the fat to coalesce and rise more rapidly than the ordinary method. Such cream is preserved in some degree from the infection of the lactic ferment, and will keep perfectly sweet many days, even in warm weather, provided always that the layer on the top is not destroyed nor disturbed; as when once this is done, especially if the top portion be mixed thoroughly with the rest, lactic fermentation is very rapid.

Ordinary, or raw cream, is either cream raised in the ordinary way, that is, by allowing the milk to rest undisturbed at the ordinary temperature; or it is separated by more modern and scientific processes, such as the action of cold and centrifugal machines. Cream, as thus produced, is a thickish, yellowish liquid, containing a variable amount of milk-fat, ranging from 12 to 50 per cent. As a rule the "solids not fat" hold in cream the same ratio to the water as in milk; and similarly the ratios between the caseine, albumen, and ash are but little disturbed, the caseine, as already remarked, being in slight excess.

The results of thirty-six analyses of cream by various chemists are thus summarised by König—

	Minimum.	Maximum.	Mean.
Milk-fat, ...	8·17	70·20	25·72
Albuminoids, . .	2·20	7·40	3·70
Sugar, ...	·74	4·57	3·54
Ash, ...	·14	3·49	·63
Water, ...	22·83	83·23	66·41

The analysis of cream presents no difficulty, and is conducted on precisely the same principles as that of milk. A little trouble

will be found in drying the cream in order to estimate the water, unless, for this purpose, quantities so small as a gramme are taken. This, spread out in a thin layer on a platinum dish, dries easily enough at the temperature of 100°. Should larger quantities for any reason be taken, it will then be necessary to treat the cream after partial drying with petroleum; extract the fat, and then dry the fat and the "solids not fat" separately—the fat at about 105°, the "solids not fat" at 100°; the loss is then considered as water. Cream can be also readily dried in a vacuum, as in the process given at p. 234.

The author has met with artificial cream, made of albumen and ordinary cream, and coloured feebly with what was probably the colouring-matter of the carrot. With a view to detect this fraud, it will be advisable, in every case, to estimate the albumen, since the albumen of milk has a tolerably definite ratio to both the caseine and the water. Thus, in the analysis of milk on p. 278, before the cream was abstracted, the proportion of milk-fat to water was as ·68 to 87·55, or ·77 to 100 of water; while, in the cream, the fat was in the proportion of ·57 to 100 of water; in other words, the values in each case fairly agreed. The ratio of the albumen, also, to the caseine, which in the milk before skimming was 1 : 4, in the cream was 1 : 5·8. In creams made up from white of eggs, &c., these relations by no means hold good; the albumen may predominate above the caseine, or be nearly equal to it in quantity. Great caution must, however, be taken in the using of certificates based solely on high albumen; for it may occasionally be a natural product, although it may well be doubted whether a cow secreting albumen instead of caseine, or in fourfold amount, is not either locally or generally diseased.

SKIM-MILK.

§ 174. Skim-milk is simply milk which has been partially deprived of milk-fat. The processes in use are somewhat various. The old-fashioned method of allowing milk to stand, and then removing the cream from the surface by skimming, is giving place, in large establishments, to centrifugal apparatus, by which a far more perfect separation of the milk-fat is effected. The composition of skim-milk compared with the milk in its original state is well seen in the following analyses by W. Fleischmann :—

	Fresh Milk.	Cream.	Skim-Milk.
Fat, .	3·64	67·63	·46
Caseine,	2·73	1·17	2·88
Albumen,	·68	·25	·49
Sugar,	4·69	2·25	5·34
Ash,	·71	·12	·72
Water, ...	87·55	28·58	90·11
Total solids, . . .	12·45	71·42	9.89
"Solids not fat," . .	8·81	3·79	9·43

Thus, by the operation the proportion of "solids not fat" has been somewhat raised, and this is constantly observed, so that the Public Analysts Society's limit of 9 per cent. of "solids not fat" is a trifle too low for skim-milk; that is, a slightly watered milk, when skimmed and sold as skim-milk, might be found up to the standard.

CONDENSED MILKS.

§ 175. A variety of "condensed milks" are found in commerce, of which the majority are simply milks dried *in vacuo* at a moderate temperature, then heated up to 100°, in order to destroy mould, and mixed with cane-sugar. There are also concentrated or condensed milks without any addition of sugar or other substance. The analysis of condensed milks differs in no respect from that of ordinary milk, save that it will be absolutely necessary to estimate the milk-sugar by copper, and then to calculate the cane-sugar either by difference or in the way given at p. 262. Unless the cane-sugar is estimated, it is not possible to calculate the amount of concentration to which the original milk has been subjected. This calculation is made by dividing the milk "solids not fat" by 9, or the amount of "solids not fat" present in ordinary milk. It is better to take this number than the higher estimate of 9·2 or 9·3;* for, in the majority of instances, it is certain that there is some decomposition and loss of the milk solids during the evaporation. The ash of the milk should also be carefully examined for alkaline carbonates. If these are present, then the probability is that an impure ash-containing cane-sugar has been employed, and if so, an exact conclusion as to the concentration of the milk cannot be arrived at. The following table gives some analyses of condensed milks, with their amount of concentration, the latter being determined by dividing the "solids not fat" column, as just stated, by 9:—

* In the original analyses by Mr. Hehner, quoted in the table, he appears to have divided by the higher number—viz., 9·3.

TABLE XIX.—COMPOSITION OF CONDENSED MILKS.

	Water.	Fat.	Albuminoids.	Milk-sugar.	Cane sugar.	Ash.	Milk solids not fat.	Condensation.	Analyst.
Anglo-Swiss Coy., made in Switzerland,	24·13	8·67	13·67	10·82	40·48	2·23	26·72	2·96	C. Karmrodt *
,, ,,	24·94	8·90	9·68	13·29	41·24	1·95	24·92	2·77	O. Hehner †
,, ,,	22·05	10·20	8·99	12·85	43·97	1·94	23·78	2·75	,,
,, made in England,	25·63	6·13	12·65	12·50	41·21	1·88	27·03	3·00	,,
,, ,,	24·99	10·88	10·02	11·92	40·23	1·96	23·90	2·65	,,
Condensed milk manufactured in Hamburg,	15·45	11·52	19·76	16·17	34·65	2·45	38·39	4·26	Schaedler. ‡
Norwegian condensed milk,	28·85	9·21	8·98	14·14	36·74	2·08	25·20	2·80	O. Hehner. *
,, ,,	29·05	9·66	8·58	12·70	38·14	1·87	22·62	2·51	,,
Helvetia,	25·29	7·19	11·73	13·01	41·04	1·74	26·48	2·94	,,
,,	26·37	6·98	11·34	13·21	40·27	1·83	26·38	2·92	,,
Gerber & Co.'s condensed milk,	23·68	9·74	9·80	12·93	41·80	2·05	24·81	2·75	,,
,, ,,	24·47	12·76	8·22	12·23	40·31	2·01	22·46	2·49	,,
Cream Milk (Hooker's process),	19·11	10·27	10·66	13·75	44·11	2·10	26·51	2·94	,,
,, ,,	18·94	11·77	10·47	13·68	42·92	2·20	26·37	2·93	,,
Nestle's Swiss milk,	15·30	8·85	9·98	13·62	50·08	2·17	25·77	2·86	,,
Mean of 10 analyses of American condensed milk (no cane sugar),	48·59	15·67	17·81	15·40	...	2·53	35·80	3·98	C. F. Chandler. § Samuel Percy. ‖

* *Dingler's Polytechnisch. Journal*, bd. 198, § 168.
† *Analyst*, vol. iv., 1879, p. 44.
‡ *Pharm. Central. Halle*, 1871, No. 35.
§ *American Chemist* (2), vol. ii., page 25.
‖ *Milchzeitung*, 1872, pp. 93 and 179.

It is obvious that by the use of the last column, the proper quantity of water to add to the condensed milk, in order to produce ordinary cows' milk, is at once seen. Thus (taking the first milk in the table), since a sample of Anglo-Swiss milk was concentrated 2·96, a pound of such milk would, by the addition of water, have to be made up to 2·96, or very nearly 3 pounds. It will be a question for the analyst to consider whether, in view of the misstatements as to the concentration of the milk to be found on many labelled tins of condensed milks, such assertions are not in their nature misleading, and whether they do not, therefore, come under the Sale of Food and Drugs Act.

KOUMISS.

§ 176. Koumiss is an alcoholic drink made by the fermentation of milk; it is prepared by the nomad population of Asia (especially by the Tartars) from the milk of the mare and that of the camel: it is also manufactured from cows' milk. The preparation of koumiss by the Tartars is very simple: ten parts of fresh warm milk, with a little sugar, are added to one part of milk which is already sour—that is, which contains lactic ferment—and the whole is allowed to rest for two or three hours with repeated stirring. The chemical changes taking place seem to be a partial decomposition of the sugar into lactic acid, the development of carbon dioxide and alcohol, and possibly certain changes in the albuminoids, changing them partly into peptones. The composition of koumiss, since it may be derived from such different sources, is variable. A few analyses are as follows:—

	Mean of ten analyses. König.	Koumiss from mares' milk. W. Fleischmann	Koumiss from cows' milk W. Fleischmann	Koumiss 48 hours old. J. A. Wanklyn.
Water,	87·88	91·53	88·93	87·32
Milk-sugar,	3·76	1·25	3·11	6·60
Lactic acid,	1·06	1·01	·79	
Caseine,	2·83	1·91	2·03	2·84
Milk-fat,	·94	1·27	·85	·68
Alcohol,	1·59	1·85	2·65	1·00
Carbonic acid,	·88	·88	1·03	·90
Ash,	1·07	·29	·44	·66

In the koumiss from cows' milk, Fleischmann separated ·166 per cent. of glycerine.

LEGAL CASES RELATIVE TO MILK.

§ 177. The following convictions are of interest :—

Appeal Case, in which the defence was, that the milk had been deprived of cream from being unintentionally skimmed by serving the customers.

This case occurred at the Liverpool Sessions, and is fully reported in the *Analyst*, 1877, p. 214.

Dr. Campbell Brown proved that the milk was deprived of its cream, the appellant affirming that the milk had been put into an eighteen-gallon can, without the slightest sophistication, and that the cream had been abstracted by serving the customers.

The Recorder said, Nobody would convince him that a milk-dealer could not, if he liked, take care that each of his customers should get a fair proportion of cream. . . . He was perfectly certain that the milk had not been skimmed, but that it had been weakened by the process of selling to the earlier customers. He was certain that when the appellant sold the milk to the earlier customers, he knew he was abstracting the cream from it—not skimming the milk, but abstracting the cream, although with no fraudulent intention. He was equally certain, too, that the appellant sold the residuum of the milk, knowing that it had been reduced to the condition in which it was when he sold it. He was quite satisfied, therefore, that an offence had been committed against the Act of Parliament. . . . The conviction was confirmed.

The officials at Somerset House have, in an appeal case, also declared their belief in the fact that milk on being served from a can, in the usual way, may have the top layer of cream entirely abstracted. The writer has always had doubts about this, for the difference of specific gravity between the cream and the solution of the other milk solids is not great, and the mere use of a dipper in serving the milk stirs it up sufficiently to render this removal improbable. We have, however, at least, *one* definite experiment on this subject.

Mr. Carter Bell states,* "One day in July I bought two gallons of milk, and analysed it, and found 100 cc. to have the composition of—

Total solids, ...	12·30
Fat, ...	2·70
"Solids not fat,"	9·60

The milk was put in the cellar, and at every hour from nine in the morning till twelve o'clock at night, one pint of milk was taken out at the commencement of each hour, and a portion of each pint was analysed. In taking out the pint, great care was taken not to stir the milk, the measure was simply dipped into the milk and taken out. The whole experiment was conducted throughout in favour of the milkman, and according to these experiments it is more advantageous for customers to be late than early."

	Total solids.	Fat.
8 o'clock in the morning,. . . .	12·30	2·70
9	12·68	3·08
10	12·68	3·08
11	12·70	3·10
12	12·70	3·10

* *Analyst*, No. 21, December, 1877, p. 162.

	Total solids.	Fat.
1 p.m.,	12·24	2·64
2 ,,	12·30	2·70
3 ,,	12·28	2·68
4 ,,	12·88	3·28
5 ,,	12·80	3·28
6 ,,	12·40	2·80
7 ,,	12·54	2·94
8 ,,	12·30	2·70
9 ,,	12·48	2·88
10 ,,	12·88	3·28
11 ,,	12·60	3·00
12 ,,	12·90	3·30

Manufacture of New Milk from Condensed.

The only interest of the following case lies in the revelation it affords of the tricks of the trade. A man was summoned by his employer, a dairyman, for adding dirty water to milk. The prisoner did not deny the accusation, but cross-examined the prosecutor, to show that the latter had been in the habit of making his men, when the milk ran short, mix with water a quantity of white stuff that was kept in the cellar, and take out to the customers to make good the deficiency in the supply of good milk. The process he called "*the fake*" of the trade. The prosecutor admitted that he kept condensed milk to make up the supply when the demand was too great, the "white stuff" referred to by the prisoner.*

Novel Defence.

A defence was set up, in a Swansea case, that the poverty of the milk was owing to its having been taken from a cow a few hours only after she had been milked dry. Mr. Morgan instituted experiments on this point. In eighteen experiments on the same cow the following results were noted:—†

Total solids—	
Highest,	17·60
Lowest,	12·59
Average,	13·93
Fat—	
Highest,	8·60
Lowest,	2·96
Average,	4·41
Solids not fat—	
Highest,	9·95
Lowest,	9·00
Average,	9·52

* *Analyst*, ii., 1878, 184.
† *Proceedings of Society of Public Analysts*, i., 1876, p. 191.

Adulteration of Milk with Cane Sugar and Water.

At the Colomb Petty Sessions, in Jan. 7, 1879, a milk-dealer was summoned for the above offence. The composition of the milk was :—

Water, ...	87·63
Milk-fat, ...	3·00
Caseine, ...	2·90
Cane sugar, ...	2·80
Milk-sugar, ...	3·10
Ash, ...	·37

The summons was dismissed on the ground (which has since become untenable) that the purchase being admittedly for analysis and not for consumption, the purchaser was "not prejudiced."—*Analyst*, 1879.

Defence that Rain had increased the quantity of Water.

In December, 1880, a cowkeeper of Hull was summoned for selling milk adulterated with 10 per cent. of water. The defendant affirmed that whilst milking the cows in the field on the morning in question, it rained very heavily, and he thought that about a pint of water fell into each of the milking buckets. The court did not consider the defence valid, and convicted and fined the defendant.—*Analyst*, 1880.

Conviction for selling "Fore" Milk.

In August, 1877, a dairy proprietor of Dublin was prosecuted for selling milk deprived of its cream. The defendant stated that it was "fore" milk, and that he had sold the "strippings" as cream. The magistrate expressed his opinion that the milk should be sold whole,—*i.e.*, with both "fore" milk and "strippings," and fined the defendant £10.*

Diseased Milk.

At the Woolwich Police Court, in December, 1875, a dairyman was convicted and fined £20 for selling diseased milk. Mr. Wigner, the analyst, proved that the sample had a peculiar colour, and that it contained no less than 13 per cent. of fat, 8·2 "solids not fat," and 20 per cent. of blood. Other witnesses proved that the defendant had a number of cows, and at least one of them was suffering from foot-and-mouth disease. There was practically no defence.†

BIBLIOGRAPHY.

The general treatises enumerated at page 43, all contain articles on milk, and may be consulted. The limits of this work preclude an exhaustive bibliography on milk—a list of the more important papers which have been consulted in the writing of the sections on milk would alone occupy more than a dozen pages. Hence it will be necessary to limit the list to the papers *which have appeared since* 1870.

* *Analyst*, i., 1877, p. 82.

† *Conviction for Selling Milk yielded by a Cow suffering from Disease.* London, 1876.

Adam, A. F.—"Étude sur les principales méthodes d'essai et d'analyse du lait," &c. Paris, 1879.
Axmann.—Ueber Milch-Verfälschung und Milch-Controlle. *Zurg. Correspond. Bl.*, 1873.
Ballard.—*Med. Times and Gazette*, 1876.
Bell, J. C.—Milk Analysis. *Analyst*, December, 1877.
Blyth, A. Wynter.—Milk of the Cow in Disease, *Chem. News*, vol. xxxii., p. 245; *Analyst*, i., 1878; *ib.* 1879, 231. Milk of the Cow in Health and Disease, *Journ. Chem. Soc.*, 1879.
Bollinger, O.—Ueber Impfs-u. Futterungs-tuberkulose, *Archiv. für Experimentelle Pathologie u. Pharmakologie.* Leipzig, 1873, 356-375.
Bollinger, O., u. Franck, E.—Gegen die grosse Gefährlichkeit des Genusses vom Fleisch u. Milch tuberkuloser Thiere. *Deutsche Zeitschrift für Thiermedizin u. vergleichende Pathologie*, 1875, t. 1.
Bouchardat, A., et T. A. Quevenne.—"Instruction sur l'essai et l'analyse du lait," 3. ed. Paris, 1879.
Cameron, A.—Analysis of the Milk of Forty-two Cows, *Analyst*, 1881.
Fleischer, M.—*Journal f. Landw.*, 1871.
Hehner, O.—Condensed Milk, *Analyst*, vol. iv., 1879.
Heisch, C.—On Diseased Milk, *Analyst*, 1878. p. 249.
Hill, A.—Milk Standards, *Analyst*, May, 1876.
Hoppe-Seyler.—"Physiologische Chemie," Berlin, 1877-80. "Handbuch der Physiologisch. und Pathologisch-chemischen Analyse," Berlin, 1875.
Kehrer.—*Centralb. f. die Med. Wiss.*, 1870, No. 33; *Arch. f. Gynakologie*, ij., Heft i. and iii.
Klebs, E.—Die künstliche Erzeugung der Tuberculose, *Archiv. für experimentelle Pathologie u. Pharmakologie*, 1 Band. 2 Heft, Leipzig, 1873, s. 177.
Klingler.—*Dingler's Polytechnisch. Journal*, 217, Augsburg, 1875, s. 343.
Kuhn, G.—*Sächsische Landw. Zeitung*, 1875.
Kuls, J.—*Pflüger's Archiv.*, xiii. 176-196.
Macadam, Dr. Stevenson.—The Quality of Milk Supplied to Towns, *Pharm. Journal.*
Macnamara, F. N.—*Chem. News*, 1877.
Milch-Zeitung—Various Papers on the Composition of Milk, &c., &c., 1870-80.
Müller, A.—*Zeitschrift f. Anal. Chem.*, 22, 129.
Muter, J.—An Ingenious Adulteration of Milk, *Analyst*, 1, 1878.
Paris, C. van.—Uebertragung der Stomatitis Aphthose der Rinder auf den Menschen durch Milchgenuss, *J. Sch. Jahrbuch*, 1873.
Pattinson.—An Abnormal Sample of New Milk, *Analyst*, 1876.
Pavesi, A., ed E. Rotondi.—*Gazzetta Chimica Italiana*, iv., 1870, 194.
Redwood, Dr.—"Notes on the Analysis of Milk," 1. 1876.
Ritthausen, H.—Neue Methode zur Analyse der Milch und über ein von Milchzucker verschiedenen Kohlenhydrate der Kuhmilch, *Journal f. Prakt. Chemie*, 1877.
Selmi, F.—*Gazzetta Chemica Italiana*, iv., 482-484; *Journal Chem. Soc.*, Lond., 1875.
Smee, J. H.—"Milk in Health and Disease," Lond., 1875.
Soxhlet, F.—Beiträge zur Physiologisch. Chemie der Milch, *Journ. f. Prak. Chem.*, 1872.
Stevenson, J.—The Decomposition of Milk, *Analyst*, 1, 1876.
Thomson, W.—The Incongruity of the Mode of Stating Milk Analyses, *Analyst*, Sept., 1877.
Vallin, E.—Le lait des Vaches Phthisiques, *Ann. d'Hygiène Publique*, 1878.

BUTTER.

§ 178. *Constituents of Butter.*—In the manufacture of butter the cream is violently agitated in a churn or other suitable apparatus, and in this manner the thin membrane* enclosing the fat globules is supposed to be ruptured. The free fat then coalesces, entangling with it some caseine and serum; the butter is well pressed together to free it as much as possible from moisture, and salt added to assist its preservation. Butter, therefore, is composed principally of milk-fat, with a small and variable quantity of water, caseine, and ash, the latter consisting chiefly, but not entirely, of the salt added.

The "*fat*" of butter consists of a mixture of the glycerides of the fatty acids—palmitic, stearic, and oleic—not soluble in water; and also of the glycerides of certain soluble and volatile fatty acids, principally butyric, with small quantities of caproic, caprylic, and capric acids. It is the association of about 7·8 per cent. of the triglycerides of these volatile acids with the glycerides of the insoluble acids, which gives to butter fat its peculiar and distinctive characters.

The different constituents, as well as the physical characteristics, of butter or milk-fat have been already described at p. 203 *et seq.*

The general composition of butter fat appears to be as follows:—

GLYCERIDES EQUAL TO FATTY ACIDS.

Olein,	42·21	=	Oleic Acid,	40·40	
Stearin and Palmitin,	50·00	=	Stearic and Palmitic Acids,	47·50	
				87·90	Total insoluble solids.
Butyrin,	7·69	=	Butyric Acid,	6·72	
Caproin, Caprylin, and Rutin,	·10	=	Caproic, Caprylic and Rutic Acids,		
	100·00	=		94·62	Total acids, calculating soluble as butyric.

Pure, dry butter fat, melted at a heat not exceeding 100° Fahr., has at that temperature a specific gravity ranging from ·91200 to ·91400; its fusing point, taken in the manner to be described, ranges from 33°·9 to 36°·5 C.

* Reasons for doubts as to the existence of this membrane are given at page 202.

The relative proportions of fat, caseine, and salt, in genuine butters, may be gathered from the following table, in which it is seen that the butter fat ranges from about 82 to nearly 87·5, the average given by Angell and Hehner being 85·45 per cent.:—

	Normandy Butter. Angell and Hehner.	A Sample of Fresh Butter. Angell and Hehner.	Butter from Isle of Wight. Angell and Hehner.	Butter from Guildford. Angell and Hehner.	Butter from Winchester. Angell and Hehner.	Mean of Eighty-nine Analyses. König.
Fat, ...	82·643	83·871	84·740	85·480	87·223	83·11
Curd, ...	5·137	2·721	3·462	2·789	2·054	·86
Salt (Ash), . .	2·915	0·424	2·089	3·151	2·108	1·19
Water, . . .	9·305	12·984	9·709	8·580	8·615	14·14
Milk-sugar, . .	...	...	...	...	...	·70

OLEO-MARGARINE,—BUTTERINE.

§ 179. Oleo-Margarine, Dutch butter, butterine, edible fat, and similar appellations, all denote different varieties of a manufactured article made expressly to imitate butter.* It is an important industry in the States, and is also largely produced in Holland (hence the name of Dutch butter) and in Belgium. As manufactured in Chicago, it would appear to be, at all events, a cleanly article. Animal life is plentiful in the States; American technical operations are on a gigantic scale, and too much capital is involved in the matter to allow of the use of any process likely to disgust the consumers. The chief constituent used is beef-fat, which consists for the most part of stearin, margarine, (so-called), and olein. The olein and margarine melt at a much lower temperature than the stearin. Mutton-fat contains more stearin than beef-fat; hence, in summer, the softness of beef-dripping as compared with the solidity of mutton-fat. This is obviously the reason why the manufacturer prefers beef-fat. The process of manufacture is briefly as follows:—The beef-fat, freed first as much as possible from fibre, passes in a very finely divided state from a sort of mincing-machine, technically called a "hasher," to large tanks, where it is melted by means of water-jackets applied to the tanks, and heated to a temperature never

* Mége Mouries, a chemist, appears to have been the first who proposed the manufacture of artificial butter. It came first into commerce about the year 1872.

allowed to exceed 39°. The result of this process is, that the fat melts to a clear yellow oil, the water and *débris* sinking to the bottom, and a thin scum of impurities rising to the surface. The latter is skimmed off, and the yellow oil run into wooden cars, in which the stearin, after a little time, begins to deposit in a more or less crystalline or granular condition; the refined fat is then put in a press-room, and kept at a temperature of from 26°·6 to 32°·2. The oleo-margarine is filtered through cotton cloths, and ultimately pressed; the result of which is, that the stearin is left behind as a white cake, and is ultimately disposed of to the candle-maker. The oleo-margarine, at this stage, is quite tasteless, and has no flavour of butter. This flavour is given by churning it with milk; lastly, the product is coloured with annatto, and rolled with ice, after which it is either made up into pounds, or packed into kegs for export. Arrived in this country, it is either sold honestly as "butterine," at the price of about a shilling per pound; fraudulently, at a higher price, as butter; or it is used as an adulterant of butter. The chemical proportions of the artificial butter vary according to the fats used in the manufacture and the details of the process employed; but they all agree in this, that when the butter is saponified and the acids set free, there is a great deficiency of soluble fatty acids, as compared with those of true butter-fat.

The average percentage composition of dry butterine-fat is as follows:—

Palmitin,	22·3
Stearin,	46·9
Olein,	30·4
Butyrin, Caproin, and Caprylin,	·4

While the proximate analysis of commercial butterine is as follows:—

Water,	12·01
Palmitin,	18·31
Stearin,	38·50
Olein,	24·95
Butyrin, Caproin, and Caprylin,	·26
Caseine,	·74
Salts,	5·22

ANALYSIS AND ADULTERATION OF BUTTER.

§ 180. The only common adulterations of butter are the substitution or admixture of fats other than butter, and of water, the latter being either left in the butter in undue proportion

through faulty manufacture, or fraudulently added. The addition of mineral substances, flour, and other articles enumerated by different writers, is at the present day very rare. The analysis of butter naturally divides itself into—(1.) The general examination and analysis; and, (2.) The investigation of the fat.

1. *The General Examination and Analysis of Butter.*—The colour, taste, and odour of the sample should, of course, be noted. It will also be found useful to examine it in thin layers microscopically. If it has been mixed by fusion with any fat, and cooled slowly, crystals may be discovered. The best way to seek these crystals is to place a minute portion of the fat on a slide, add a drop of castor or olive oil, press the thin disc of covering glass so as to get a very thin layer, and examine by polarised light. Under such circumstances, if crystals should be present, there will be seen dark crosses similar to those in potato starch. Such crystals are suspicious, because they show that the butter has been melted; and it certainly must be a most unusual process to melt butter save for the purpose of mixing with other fats. The rare adulteration of any other substance, such as starches, &c., by mechanical admixture, cannot fail to be detected by the microscope.

The Proximate Analysis of Butter—that is, the separation of butter into mineral matters, caseine, butter-fat, and water, is very readily performed.

10 to 20 grms. of the butter are weighed into a counterpoised porcelain dish, and melted over a low gas flame, keeping the butter at any temperature between 105° and 110°, with constant stirring, until all effervescence has ceased. (By using a thermometer as a stirrer this is easily effected.) The weighing of the dish and its contents when cool, subtracted from the first weight, gives the loss equalling the water, and it may be worked into percentage. Keeping the butter for a considerable time at 100°, or above, must be avoided, for it increases the weight. The following is an experiment by Dr. Milne:—

Pure butter-fat weighed, ...	30·1840 grms.
,, after half an hour heating in the water-bath, .	30·1832 ,,
,, after two hours, . . .	30·1864 ,,
,, after one hour at 110° .	30·1984 ,,
,, after one hour rising to 116°, . . .	30·2036 ,,

The above method has the merit of expedition, and it is tolerably accurate; but the water may also be estimated by placing about 1 grm. of the butter fat in a large platinum dish, so that the fat forms a thin layer, and then exposing it to the heat

of the water-bath until it ceases to lose weight. The fat is next melted from the curd and salt (both of which settle to the bottom), and is poured off as far as possible, the residue being thoroughly exhausted by boiling benzine, ether, or petroleum, which can be effected, if care is taken, in the same dish without transference to a filter. On now weighing, the loss equals the fat. Lastly, the curd is burnt away at a low red heat, and the ash weighed.

The general analysis finished, it remains to consider the results :—

(1.) *Fat.*—The fat should not be below 80 per cent.; any figure under this should justly be considered evidence of adulteration.

(2.) *Water.*—There is no standard followed or fixed with regard to the percentage of water. In those cases in which the fat is below 80 per cent., the deficiency of fat is usually from excess of water; and seeing the variable quantity of water found in butter, it is wisest not to certify on the ground of water alone, unless there is sufficient to lower the percentage of fat below 80 per cent.

(3.) *Caseine.*—The average quantity of caseine is 2·5 per cent., but it may reach 6 to 7 per cent., and the higher the percentage of caseine the less likely is a butter to keep, although this usually is evidence of error in the manufacture rather than of adulteration.

(4.) *The Ash.*—This should consist of common salt and phosphate of lime. Butter is said to be adulterated occasionally with sodium silicate, and therefore the ash should be fused with sodic carbonate, dissolved in hydrochloric acid, evaporated to dryness, and dissolved in water. Any residue will consist of silica. If other mineral adulteration is suspected, a complete analysis of the ash may be necessary (see p. 100). There is no definite standard fixed with regard to the weight of the ash, but most chemists agree that it should not exceed 8 per cent.

The following are a few examples of adulterated butters, the adulteration being detected simply from the proximate analysis :—

	Devon Butter.	Devon Butter.	A Sample of Butter. (Angell and Hehner.)	A Sample of Butter. (Angell and Hehner.)
Fat, . .	78·50	76·34	67·580	47·019
Caseine, . .	1·72	6·60	6·880	7·854
Water, . .	17·10	13·36	23·981	42·358
Salt, . .	2·68	3·70	1·559	2·689

2. *Examination and Analysis of the Fat.*—By far the most important process in butter analysis is the examination of the fat. The data by which the analyst judges whether a butter consists of foreign fats entirely or partly, are derived from—(*a.*) The pattern of the melted fat when dropped on water; (*b.*) certain simple tests; (*c.*) the melting-point; (*d.*) the relative proportion of soluble and insoluble fatty acids. For many of these tests, the first requisite is a pure dry fat. This is easily accomplished by melting a sufficient quantity of the butter over the water-bath. In a short time the water, curd, and salt, sink to the bottom, and the nearly pure fat can be poured off. Should it not be clear, it must be filtered through filtering paper or glass-wool. This operation will necessitate the filter being kept warm in a suitable steam-jacket.

§ 181. (*a.*) *The Author's Pattern Process.*—In the winter of 1880 the author made various experiments on butter-fat, and discovered the curious fact that all solid fats, when melted and dropped on to water, the temperature of which is low enough to ensure their solidification, set in a definite form or pattern. To attain success, it is necessary that the fat as well as the water be of a certain temperature; but with many of the glycerides and mixtures of glycerides, such, for example, as butter, butterine, dripping, &c., the range is very wide; so that if the fat is perfectly fluid, and within one or two degrees of 100°, the water ranging from 0° to 15°, a pattern more or less perfect is obtainable.

Each fat appears to have its own distinctive pattern, and can be identified by its pattern alone. On the other hand, each fat has a variety of patterns, for every alteration of the experimental conditions modifies more or less the form of congealed drops. If, however, the conditions under which each experiment is performed are precisely similar, then there is no difficulty in obtaining the same form, or at least very similar forms, any number of times.

The chief modifying conditions are the difference of temperature between the fluid fat and the water, and the height from which the fat falls. I have found that from 3 to 4 inches is the best height, and that a greater fall than this tends to spread the films out, and renders all patterns more or less similar.

Referring to individual forms—

Butter.—The experiments were made on several samples of butter, whose genuineness had been proved by analysis. The fat was melted and filtered, and kept in an air-bath at temperatures of from 40° to 80°, and then dropped from a clean warm glass rod on to water of from 10° to 15°. The most common and distinctive form attained in this way was that of a beautiful

foliated film, not unlike the leaf of a pelargonium. The film may be transferred direct to the lithographic stone, and one may thus have a direct impression and a permanent record. The details of delicate veining are, as might be expected, lost. The best pattern temperature for butter is 55°, the water being at 10°; but regular forms may be obtained up to 100°. At higher temperatures success is rare. I found that although butter of 40° to 50° when dropped on to water of 10° sets in a radiated star form, yet when dropped on to water of 8°, although momentarily there was a beautiful complicated foliation with many radiating wings, these wings suddenly mutually repelled each other, and the pattern fell, or rather flew to pieces. Glass plates were prepared chemically clean by first treating with alcoholic soda and then washing them with ether; the plate was next dipped into water, and thus a thin water film obtained. On this perfectly smooth wet surface, butter and other fats were dropped. In the case of butter, the pattern lost much of its beauty, but was always very regular in outline. Butter films are of extreme tenuity, and although several attempts to photograph them were made, the light passed through almost as perfectly as through glass, therefore the photographic shadows were too indistinct to make any use of.

Butterine.—The various mixtures of animal fats in the market known as butterine, or artificial butter, give by no means identical patterns, for they vary much in composition; but in each case the form can be distinguished from the butter films, and from the pattern alone it is always possible, and often very easy, to say whether a given film is butter or not. The best method to distinguish the artificial from the genuine product, is to take pure butter-fat and the suspected sample, and after melting them each at the same temperature, to drop them on to the same glass plate side by side: the butterine pattern is full of minute crystals; the butter pattern has no crystals. The pattern of one sample of butterine was found to be identical with that of tallow—little white dots containing bunches of crystals (see the photograph, No. 1, *Tallow*).

Tallow.—One form of tallow pattern has just been alluded to. It is the most common form when melted tallow falls on water. This fat of high melting point is a good illustration of the many forms which may be produced at different temperatures. Thus, at 0° the fat sets on water in circular indistinct drops, but when more fluid, and dropped on glass, its pattern is distinct and crystalline.

Paraffin, giving no pattern by itself, when mixed with other animal fats, as may be expected, profoundly modifies the film.

Equal parts of paraffin and stearic acid, for example, give by suitable treatment a pattern in the shape of a broad cross. With reference to the fat patterns of spermaceti, stearic acid, and generally fats of high melting points, it need scarcely be said that it is impossible to obtain them by dropping the fat on to *cold* water. Such a proceeding only gives a shapeless mass. To be successful it is absolutely essential that the water of the glass plate should be warm. For example, spermaceti gives no definite form when melted at 100°, and dropped on to cold water, or even water of 50°; the water must be heated up to 80° or 90° for a good result to be obtained. Very beautiful lace patterns are produced by wetting a warm glass plate with absolute alcohol, and dropping tallow, stearic acid, or spermaceti upon it; all the finer portions of the film are at once dissolved, while the veins and denser portions remain, reminding one of skeleton leaves (see photograph No. 2, *Spermaceti*); the thin films of butterine, dripping, and similar substances will not stand this treatment, but are at once dissolved.

§ 182. *Cohesion Figures.*—Tomlinson (*Phil. Mag.*, 1861 and 1862), some years ago, drew attention to the peculiar cohesion figures of various liquids and oils; but the patterns of the solid fats, when melted and dropped on to warm water, do not appear to have received any consideration. The author finds, however, that each solid fat behaves differently, and may also in this way be identified, and any admixture generally be correctly surmised. Should the water be at such a temperature as to keep the fat very fluid, it rapidly spreads over the surface of the water, breaks up into lacunæ, shows a beautiful iridescence, and the phenomena are over so rapidly as to leave but little impression on the memory. The author, therefore, prefers to operate at temperatures just sufficient to keep the fat a little fluid, so that the action takes place in a slow, regular, and methodical manner. As an example, one experiment may be detailed. Filtered pure butter-fat, butter adulterated with 5, and with 10, per cent. of lard, and lard itself, were all put in the same air-bath and brought to 55°·5. A large flat dish made chemically clean was filled with water of 44°, and a single drop of each of the four fats was dropped simultaneously on the surface of the water, and their behaviour noted. The butter-drop immediately spread itself out into a thin film, became agitated by a rapid circular motion, and threw off minute droplets of butter-fat. The motion gradually ceased, the drop extended itself, became irregular in outline, crenated at the edges, and then contraction took place. At this stage its appearance was that of an irregular square, surrounded by small circles at distances from the central square and from each

other of some three diameters. Both butter-drops containing 5 and 10 per cent. of lard respectively, flattened out with extreme slowness, were agitated by a gyratory motion, threw off no droplets of fat, and ultimately also broke up with extreme slowness. It was noticed that the 5 per cent. drop was thinner and larger than the 10 per cent. The drop of lard underwent no alteration, remaining circular and quiescent up to the moment of solidification.

(*b.*) *Other Simple Tests.*—The processes just described require little apparatus and skill, and still less is needed in the following test proposed by Hager * :—A bit of wick is inserted into melted butter, lighted, and then blown out. If the butter is pure there is little odour, but if artificial a strong tallow-like smell is at once perceived.

A test similarly dependent upon odour, is to add a small quantity of the butter to a mixture composed of 1 volume of pure concentrated sulphuric acid, and 2 volumes of 95·98 per cent. alcohol, and to distil; the first two or three cc.'s are collected and rubbed in the hands; the odour is buttery or tallowy according to the purity of the sample.

Donny has also recommended an easy test: a little of the sample is heated in a test-tube; pure butter froths or foams much, and becomes brown in colour. If it is composed of foreign fats, there is but little foaming; the liquid may, however, bump violently, and masses of caseine become brown, while the fat itself remains with but little colour.

W. G. Crook † has experimented upon the solvent action of carbolic acid on butter as compared with other fats. 1 grm. of purified butter-fat is put in a test-tube and liquefied, 2½ cc. of carbolic acid solution (10 acid, 1 water) are added, after which the mixture is shaken, and then put on one side for a little time. If the sample is pure butter, it wholly dissolves; if beef, mutton, or pork-fat is present, the mixture will resolve itself into two solutions of different densities, with a clear line of demarcation. If beef-fat, the lower layer will occupy about 49·7 per cent. of the total volume; lard, 49·6; and mutton, 44·0. W. Lenz has also tried this process, and generally confirms the results obtained by Mr. Crook.‡

* H. Hager: *Pharm. Central. Halle*, xviij. 413.

† *Analyst*, 1879, 1111.

‡ *Zeitschrift für Analyt. Chemie*, 1880, 370. C. Husson (*Compt. Rend.*, 85, 718) has proposed an ancient test depending on the different solvent properties of alcohol for margarine, &c.; and F. Filsinger has a very similar method (*Pharm. Central. Halle*, xix., 42). Both these tests, however, are of little practical value among such a number of positive reactions.

§ 183. (*c.*) *The Melting-Point.*—Various methods have been proposed for the determination of the melting-points of fats. The one used by most analysts is to take the melting-point in a fine tube. A piece of quill-tubing is drawn out, so as to make a tube about the diameter of a knitting needle, and from two to three inches in length. The fat is now drawn up to the extent of about an inch, and permitted to solidify. The tube thus charged is placed in some cold water in a small beaker, which is "nested" in a second beaker, a little water being between the two, the inner beaker carrying also a thermometer. Heat is now applied, and the moment the fat runs up the tube the temperature is noted. A modification of this process* is to take a short capillary tube, blow a bulb on it, and while the bulb is still hot, plunge the open end into the melted fat; let it run up a short distance, and then solidify the fat by the application of cold. To take an observation, the tubes are placed in water, so that the bulb is uppermost; on melting, the fat runs up into the semi-vacuous bulb, and this rise is somewhat more easily observed than in the simpler process.

Another method is the employment of a little bulb weighted with mercury, so as to weigh from 3 to 4 grms.; the bulb rests on the surface of the fat in a test-tube, which is immersed in a beaker of water provided with a thermometer, and the moment the bulb sinks is noted. A modification of this is the employment of a light float sunk to the bottom of the fat, and retained there until it is solid; on now applying heat, the float rises at a certain temperature, which is taken as the melting-point. The melting-point of various fats is as follows:—

Butterine,	31°·3C.
Cocoa Butter,	34°·9C.
Butter (average),	35°·8C.
Beef-dripping,	43°·8C.
Veal-dripping,	47°·7C.
Mixed,	42°·6C.
Lard, from	42°C. to 45°C.
Ox-fat, from about	48°C. to 53°·0C.
Mutton-fat, from about	50°C. to 51°·6C.
Tallow,	53°·3C.

It hence follows that a low melting-point indicates the probable presence of butterine, especially that form which is partly manufactured from a concrete oil, obtained from the seeds of *Garcinia Indica,* and is known under the name of Mangosteen oil, or kokum butter. A higher melting-point indicates, as a probable adulterant, dripping, lard, or other animal fat.

* O. Kellner, *Zeitschrift fur Anal. Chemie,* xx. 1.

Specific Gravity.—The method of obtaining the specific gravity of butter-fat is to fill a counterpoised specific gravity bottle, provided with a thermometer stopper, of 50 to 100 grms. capacity, with water of 35° (95° Fahr.), and immerse it in a beaker of water of about 43° (109°·4 Fahr.) By thus heating the specific gravity bottle by a liquid which is falling in temperature, the water in it can be brought exactly to 37°·7 (100°Fahr.), at which temperature the bottle is taken out, slightly cooled and weighed; and in this manner the weight of that particular bulk of water at 37°·7 (100° Fahr.) is obtained, and this value used for the subsequent operations. To take the specific gravity of the fat, the pure filtered fat, at 35° (95° Fahr.), is poured into the clean dry bottle, and the exact process just detailed followed.

The specific gravity, as first pointed out by Mr. Bell, of Somerset House, has a direct relation or correspondence to the percentage of insoluble acids, a fact, it must be remembered, only applicable to pure unadulterated butter-fat. Thus—

Specific Gravity at 37°·7 (100°F.)	Actual Insoluble Acids Found. Per cent.
·91382	87·47
·91346	87·89
·91337	87·98
·91290	88·48
·91286	88·52
·91276	88·62
·91258	88·80
·91246	89·00*

The fats used for the adulteration of butter are of low density. Vegetable butterine has a specific gravity ·90294; dripping, ·90659; so that a low specific gravity—that is, anything below ·91101—is strongly indicative of foreign fat.

Instead of the above method, which requires a considerable quantity of material, the density may be approximately taken by the well-known specific gravity bubbles, a process which we owe to Mr. Wigner. If the butter-fat be placed in a wide test-tube, and a bubble of the specific gravity, say of ·896, be kept just beneath the surface by a thermometer passing through a cork in the mouth of the tube, at a certain temperature the bubble will slowly sink to the bottom. In butters of ·911 density, above which a sample may be passed, beads will sink as follows:—

Specific gravity of beads,	·8890	·8896
Temperature, . .	62°·7 (145°F.)	55°·5 (132°F.)

* Muter, *Analyst*, i., p. 7, 1877.

If the beads sink at any temperature lower than these, the butter will need further examination by actual determination of the fatty acids. As a guide to the gravity, it may be assumed that a difference of one degree in the sinking temperature indicates ·30 actual density, equal to about ·35 per cent. fatty acids, and nearly 5 per cent. of foreign fats.* From some experiments by Mr. Jones it would seem that the specific gravity of butter increases with age.†

§ 184. *Direct Titration of Butter by Alcoholic Potash.*—This elegant test was first suggested by Dr. Koettstorfer, and is a general method more or less applicable to all fats, but especially suited to butter-fat, for most other fats contain only the higher fatty acids, and the lower acids having a smaller molecular weight, butter must contain more molecules of acid than equal weights of another fat—in other words, requires more potash for saponification. Koettstorfer used semi-normal hydrochloric acid and an alcoholic solution of potash; this alkaline solution being about the same strength as the acid, the indicator was a dilute alcoholic solution of phenol-phtalein. From 1 to 2 grms. of the purified filtered fat are weighed in a tall beaker of about 70 cc. capacity, 25 cc. of the potash solution are added, and heated in a water-bath. When the alcohol is nearly boiling, the mixture is stirred with a glass rod till all the fat is dissolved, which does not take more than a minute. The glass rod is washed with a little alcohol, and the beaker covered with a watch-glass, and heated further for 15 minutes, in such a manner that the alcohol does not boil too violently. At the end of the quarter of an hour, the watch-glass is washed with spirit, and the alcoholic solution is stirred for one minute longer with the glass rod before used, so as to saponify any fat that may still adhere to it. The solution is now taken from the water-bath; 1 cc. of alcoholic solution of phenol-phtalein added, and it is titrated back with semi-normal hydrochloric acid. The exact point is very sharply indicated by the phenol-phtalein changing from a crimson to a yellow. (This reagent is very sensitive to CO_2; it is therefore better to use a flask than an open beaker.) Thirteen butters heated in this way by Dr. Koettstorfer used for every grm. of fat from 221·5 to 232·4 mgrms. of KHO.

* A method of taking the specific gravity of fats recommended by Mr. Estcourt (*Chem. News*, vol. xxxiv., p. 254) deserves notice. The bulb of a Westphall's balance is suspended in a test-tube containing the fat, the test-tube itself is immersed in a metal tube containing paraffin, and secured in a water-bath; when the paraffin-bath shows a temperature of 92°·2 (206°Fahr.), the weights are adjusted.

† *Analyst*, 1879, 39.

On the other hand, there is a wide difference between this amount and that required by other fats, the following being about the saturation capacity in mgrms. of potash for 1 grm. of various fats:—

	Potash KHO. Milligrammes.
Oleo-margarine,	195·5
Beef-dripping,	196·5
Tallow,	196·8
Lard from kidneys,	195·8
Lard from unsmoked bacon,	196·7
Commercial lard,	195·0
Dripping,	197·0

Or if the suggestion of Mr. Allen* be accepted, and the results be translated into equivalents of the fat by dividing 56·1 by the mgrms. of potash, the results are as follows—

Oleo-margarine,	286·5
Beef-dripping,	285·5
Tallow,	285·1
Lard from kidneys,	286·5
,, ,, unsmoked bacon,	286·7
Commercial lard,	287·1
Mutton dripping,	284·8

The chief convenience in expressing the number in equivalents is, that it then becomes a matter of indifference whether potash or soda† is used for the saponification. The practical question in the use of this test is: what is the lowest limit above which a butter may be passed as genuine, but below which it will be necessary to examine the butter by other means? The general opinion of analysts as to this point is, that butter-fat, 1 grm. of which uses less than 226 mgrms. of KHO (equivalents 248·2), is probably adulterated. The formula for calculating the amount of admixture which has been proposed is

$$(227 - n) \times 3{\cdot}17 = x.$$

x being the percentage of admixed fat, n the number of mgrms. of potash used.

§ 185. (*d.*) *The Decomposition of the Fat into Fatty Acids and Glycerine.*—This is effected by saponifying with an alcoholic solution of potash, decomposing the soap with sulphuric acid, washing the subsequent fatty acids with water, titrating the soluble, and weighing the insoluble acids. The details of the process have been so simplified by successive improvements, that what was formerly a tedious and even difficult operation, is now

* *Analyst*, 1879, 162.

† It is scarcely necessary to add that should soda be used, then 40, the equivalent of soda, must be divided by mgrms. of the alkali used.

moderately speedy and simple. The solutions requisite are as follows:—*

(1.) Approximately semi-normal alcoholic potash solution, 28 grms., roughly weighed, of KHO, dissolved to a litre with alcohol; specific gravity ·840.

(2.) Approximately semi-normal sulphuric acid—*i.e.*, 25 grms. of the strong acid to the litre.

(3.) Deci-normal soda solution of exact strength, most conveniently made by dissolving metallic sodium in water, in the exact proportion of 2·3 grms. to the litre. [1 cc. equals ·0088 of butyric acid.]

It is necessary to know with the greatest exactitude the relationship between the potash and the sulphuric acid solution; the exact quantity of alcoholic potash that is to be used in the analysis is delivered from a 25 cc. or 50 cc. pipette, as the case may be, phenol-phtalein solution added, and then titrated by the acid. It is also necessary to know the relationship between the d. n. soda and the sulphuric acid, which must also be found in the usual way. 4 to 5 grms. of the pure dry fat are weighed by difference into a flask, and 50 cc. of potash solution added; the flask, closed by a glass marble, is now heated on the top of the water oven, and by occasionally giving it a rotatory motion, saponification is complete under the hour at the low temperature of 50°

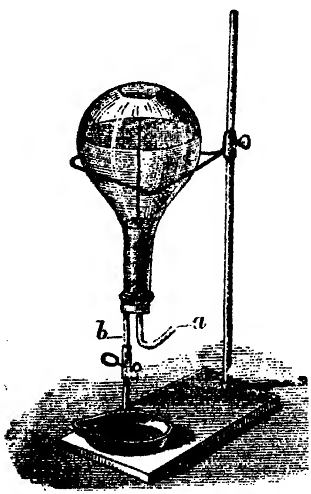

Fig. 27.

The author does not himself follow the above process, but uses the strong small assay flasks recommended by Dr. Dupré. These flasks are of about 70 cc. capacity, and with rather long narrow necks, the whole capable of bearing considerable pressure. 4 to 5 grms. of the fat are poured into such a flask, 25 cc. of potash solution added, well corked with a caoutchouc stopper, which must be secured by string and strong linen or canvas, and then the flask suspended in the boiling water of a water-bath. At the end of an hour or less it may be taken out completely saponified.† When cool the flask is opened, the soap gently melted and poured into

* "Butter-Fat," by E. W. Jones, F.C.S. *Analyst*, May, 1877.

† The reason for preferring this method is, that less potash is required.

a flask of about 500 cc. capacity, having a long, rather narrow neck (see fig. 27), which carries the tubes *a* and *b*—the tube *a* for the admission of air, the tube *b* furnished with a stopcock. In this flask the soap is decomposed by adding about 1 cc. more sulphuric acid than is necessary to neutralise the potash; if, for example, the latter is neutralised by 25 cc. of the sulphuric acid 26 cc. are added, and after this addition the fatty acids melted so as to form a layer on the surface of the acid water. At this point the whole may be diluted with warm water up to 200 cc. or 300 cc., the cork carrying the tubes inverted, and the flask turned upside down, as represented in the figure. After standing a few hours the cake is more or less solid, and the lower stratum of liquid may be run off almost clear. It will, however, always be safest to pass it through a filter. By adapting an india-rubber tube to *a*, warm water may be sucked up through *b*, and the fat washed in the flask (perfectly closed by pinching the india-rubber), and then the cake allowed to form as before. The fluid is now again run off from the solid, and this time cold water may be sucked up through *a*, and the whole process of alternations of hot and cold water repeated. Lastly, the cork with its tubes is removed, any adherent fat washed off with warm water into the flask, the latter adapted either to an upright Liebig's condenser and boiled, or connected in the usual way with a Liebig, which has as a receiver a flask, adjusted by a cork tightly to the bent tube of the condenser, and is furnished with a mercury valve, the whole forming a closed system. In the latter case, also, the heat is applied to boiling for five or ten minutes, and the distillate added to the filtrates; lastly, the cork with tubes is again connected, the flask inverted, the liquid when cool run off, and the fat finally washed with a little cold water and allowed to drain.

The watery liquid contains sulphuric acid, sulphate of potash, alcohol, butyric, and the other soluble fatty acids; it will be in bulk from 600 to 700 cc., and may be made up to any definite quantity. In any case, a portion of it—a quarter, a fifth, or even a tenth—must be taken and titrated with d. n. soda, which, when the quantity required to neutralise the 1 cc. of sulphuric acid in excess is subtracted, indicates the amount of soluble acid, and is always returned as butyric, which is near enough to the truth.

Instead of this method it may be useful to titrate the acid liquid, distil until all the volatile acid which can be obtained has gone over, and then titrate the distillate. It is also possible to separate the volatile fatty acids from such a solution by shaking up with ether in the tube figured at p. 69, the ether dissolving the acids freely.

The *insoluble fatty acids* remaining partly in the flask, with a trace on the filter, are now united in a flat porcelain dish. This is done by melting the acids in the flask, pouring off, and extracting by alcohol and ether—the same solvent also dissolving the acids from the filter. On evaporation of the alcohol and ether, one or two large bubbles of water may be formed in the acids, and it is best to add a few drops of absolute alcohol. The dish is now placed on the top of the water-bath (the water in which should only boil gently), and weighed at short intervals; if after twenty minutes only 1 or 2 mgrms. are lost, the weight is considered constant.

Reichert has modified this process: the same quantity of butter is taken each time, saponified, decomposed, and distilled in a weak current of air. The details of the process are as follows:—2·5 grms. of the anhydrous fat are saponified with alcoholic potash [1 grm. KHO in 20 cc. alcohol of 80 per cent.] After saponification 50 cc. of water are added, and 20 cc. of diluted sulphuric acid [strength 10 per cent.], the mixture is then distilled in a weak current of air; the distillate, which mostly contains some of the fixed fatty acids, is filtered through wet filter paper into a 50 cc. flask, the distillate made up to exactly 50 cc., and titrated. Thirteen pure butters on experiment took 13 to 14·9 cc.'s of decinormal soda; cocoa-nut fat, 3·70; oleo-margarine, 0·95; lard, ·30; kidney fat, ·25; rape oil, ·25. Butter-fat and lard, melted together and mixed as follows, required the following cc.'s of decinormal soda to neutralise the distillate—

Percentages of butter in the mixture,	p.c. 0	p.c. 20	p.c. 40	p.c. 60	p.c. 80	p.c. 100
cc. decinormal soda, . .	0·30	3·10	5·90	8·50	11·50	14·30
Difference, ...		2·80	2·80	2·60	3·00	2·80

From these and other results Reichert thinks the percentage of butter may be found in a mixture by the following formula—

$$\text{Percentage butter} = (7·30 \pm 0·24)\,(n - 0·30).$$

n being the number of cc.'s of d. n. soda used in titrating the distillate.

L. Medicus and S. Scherer* have examined the process of Reichert, and given a decided verdict in its favour. They have also examined by the process, whether the melting of butter is accompanied by any separation of its constituents, and their experiments appear to prove that there is in point of fact a

* *Zeitschrift für Analyt. Chemie*, 1880, p. 159.

considerable subsidence of the heavier fats. Thus, a kilogram. of pure butter was allowed to cool slowly after melting in a capacious vessel, with constant stirring; when a sample was taken, and the distillate obtained after Reichert's method used, 14 cc. of d. n. soda. The same butter was then remelted, and allowed to cool slowly without stirring, and samples taken from various portions with the following results :—

	D. N. Soda. cc.
Mixture,	14·0
Upper layer,	13·3
Under layer,	14·2
Outer layer near the side,	14·4
Inner middle layer,	17·3

The same chemists, applying Reichert's method to various fats, obtained the following results :—

	D. N. Soda. cc.
Butter-fat,	13·6 to 14·0
Lard,	·2
Rape oil,	·3
Sesame oil,	·35
Olive oil,	·3
Palm oil,	·5

A distillation process was proposed in England before the publication of Reichert's paper by Mr. Perkins :* a solution of oxalic acid was used to decompose the soap, and all the volatile acids were supposed to distil over; but the test experiments given are rather below the total amount which were probably present. There is one advantage of a distillation process which must not be lost sight of—viz., the acids may be identified by fractional titration when treated after Duclaux's process, described in the article on "Wine."

A process of saponification has been proposed and practised by Mr. West Knight,† which is based on the insolubility of the oleate, stearate, and palmitate of barium, and the ready solubility of the volatile fatty acid combinations with barium. The butter-fat is saponified with alcoholic potash in the ordinary way. The soap solution is diluted to 300 cc., and a solution of chloride of barium added until a curdy precipitate separates, and the liquid is no longer rendered milky by a fresh addition—the insoluble barium fatty acids are collected on a filter, and ultimately transferred to a tube such as is used by Muter (p. 302), and the fatty acids liberated by sulphuric acid and shaken up with ether;

* *Analyst*, 1879, 142. † *Analyst*, 1880.

when separation has been effected, a fractional part of the ether is taken, and evaporated in a tared flask.

Further Analyses of the Insoluble Fatty Acids.—The insoluble fatty acids are, as already stated, oleic, palmitic, and stearic; it is their total weight which is alone valuable, and to separate the three with accuracy is not easily effected. The first can, however, be very readily isolated by the following process, the details of which have been worked out by Dr. Muter. The process depends upon the well-known fact that the oleate of lead, $Pb2C_{18}H_{33}O_2$, can be separated from plumbic palmitate, $Pb2C_{16}H_{31}O_2$, and plumbic stearate, $Pb2C_{18}H_{35}O_2$, by taking advantage of the solubility of the former in ether.

About 1 grm. of the fatty acids is combined with potash, and the solution well diluted with boiling water, and carefully treated with acetic acid added to the boiling solution until a permanent turbidity is produced; solution of potash is now dropped in with constant stirring, until the liquid just clears again. The solution is now precipitated by plumbic acetate in slight excess, and is stirred until the precipitated soap settles thoroughly. The supernatant liquid is poured off, and the soap once washed by boiling with a large volume of water and decanting; plumbic oleate, palmitate, and stearate are thus obtained as perfectly neutral salts, the first being soluble in ether, the last two quite insoluble. The lead soap is now transferred to a flask of 100 cc. capacity, and the plumbic oleate dissolved out by ether, the ethereal solution being passed through a filter. The end of the process is known by the washings ceasing to blacken ammonium hydrosulphide. The filtrate and the washings should not exceed 200 cc., a fractional portion of which may be evaporated to dryness in a platinum dish, and weighed as plumbic oleate. To ensure perfect accuracy, the remainder should be ignited and weighed as $Pb + PbO$; the residue treated with acetic acid to take up the PbO, and the residual Pb calculated to PbO. By deducting the weight of plumbic oxide thus obtained from the total plumbic oleate, and allowing for the hydrogen displaced, the oleic acid is obtained.

Dr. Muter recommends, however, an easier method. This requires a long graduated tube of 250 cc., having a well-ground stopper and a stopcock, which is placed at 50 cc. from the bottom. The ethereal solution is placed in this, the soap decomposed by hydrochloric acid [1 : 2]; and (when the chloride of lead is fully settled) a known quantity of the supernatant ethereal solution drawn off, evaporated, and weighed as oleic acid.

In the majority of adulterated butters, the specific gravity, the melting-point, and the fatty acids are all widely different

from that of genuine butter, so that there is no room for doubt. Occasionally, however, a butter may be met with in which a small proportion only of foreign fat has been used, and in such a case the analysis must be repeated several times lest a mistake be made. Of all the above determinations, the percentage of insoluble and soluble fatty acids is of the greatest importance. A marked deficiency or complete absence of soluble, and an increase of insoluble, are the characteristic features of fats other than butter.

The following are a few examples of percentages of fatty acids found in genuine butters :—

	(1.)	(2.)	(3.)	(4.)
Soluble, . .	5·92	5·76	5·37	4·77
Insoluble, .	87·86	88·10	87·68	88·44
	93·78	93·86	93·05	93·21

It is generally accepted that 88 per cent. of insoluble acids, if associated with 6·3 of soluble acids, is a fair standard of butter calculation, and that if a butter shows anything less than 89·5 insoluble, with 5 soluble, it may be passed as genuine.*

A few examples of adulterated butter-fat are as follows :—

	(1.) A Commercial Butter.	(2.) A Commercial Butter.	(3.) Butterine.
Soluble, . .	1·98	2·34	·58
Insoluble, .	93·30	93·82	95·51
	95·28	96·16	96·09

LEGAL CASE.

Somerset House standard for water in butter.

At the Bath Police Court (January, 1879), a dairyman had been summoned for selling butter, the proximate analysis of which showed a considerable addition of water. An appeal to Somerset House elicited the following certificate :—"We hereby certify that we have analysed the butter, and declare the results of our analysis to be as follows :—

	Per cent.
Water, ...	23·27
Butter-fat, ...	74·69
Curd, ...	1·26
Salt, ...	·78

"The results of our analyses of numerous samples of ordinary commercial butters obtained from different parts of the country, including the south of England, show that the proportion of water present is very variable, and that it occasionally amounts to as much as 19 per cent."

* Muter, *Op. cit.*

BIBLIOGRAPHY.

ANGELL, G., and HEHNER, O.—"Butter: its Analysis and Detection." 1st. ed., Lond. 1874; 2nd ed., 1878.

BLYTH, A. WYNTER.—Easy and Rapid Method of Manipulating the Fatty Acids. *Analyst*, ii. 1878.

———On the Figures or Patterns which Liquid Fats assume under certain Conditions. *Analyst*, 1880.

CROOK, W. G.—A New Method of distinguishing Butter from some other Fats. *Analyst*, 1879.

DIETZEL, u. M. G. KRIESNER.—*Zeitschrift f. An. Chem.*, 1879.

DUPRÉ, A.—The Composition and Analysis of Butter-Fat. *Analyst*, 1, 87, 114.

HAGER, H.—*Pharm. Central. Halle*, xviii., 413.

JONES, E. W. T.—Butter-Fat: its Analysis and Composition. *Analyst*, ii. 1878, 19, 87; Influence from the Decomposition of Butters through Age on the Specific Gravity of the Fat, &c. *Analyst*, 1879.

KOETTSTORFER, J.—Neue Methode zur Untersuchung der Butterfett auf fremde Fette. *Zeitschrift f. Anal. Chem.*, 1879, 199, 431. *Analyst*, 1879, p. 106.

KRETSCHMAR, M.—*Deut. Chem. Ges. Ber.*, x. 2091-2095.

MEDICUS, L., u. S. Scherer.—*Zeitschrift f. Anal. Chem.*, 1880, 159.

MILNE, J. M.—Notes on the Analysis of Butter. *Analyst*, 1879, 40.

MUTER, J.—Butter Analysis. *Analyst*, 1877, p. 7.

PERKINS, F. P.—*Analyst*, 1879, 142.

REDWOOD.—On the Determination of the Melting-points of Butter and other Fats. *Analyst*, 1, 1877.

REICHERT, E.—Butter-Prüfung nach Hehner's Princip. *Zeitschrift f. An. Chem.*, 18, 64.

WEST-KNIGHT, E.—On the Estimation of the Insoluble Fatty Acids in Butter-Fat. *Analyst*, 1880, 155.

WIGNER, G. W.—On Estimation of the Gravities of Fats. *Analyst*, 1, 1877, 35.

———On Butter Analysis by Koettstorfer's Process. *Analyst*, 1879, 132.

———On Butter-Fat, and Ratio of Expansion by Heat. *Analyst*, 1879, 183.

BUTTERMILK.

§ 186. Buttermilk is the thin whey left behind when the fat has been extracted in the process of butter-making. It is never fat-free; it contains all the constituents of milk, but a great portion of the sugar has been changed into lactic acid. It is then essentially a dilute, poor acid milk.

The average composition of fresh buttermilk is :—

Water,	90·62
Caseine,	3·78
Fat,	1·25
Milk-sugar,	3·38
Lactic acid,	·32
Ash,	·65

The lactic acid tends ever to increase, so that samples which have stood a little time will contain more lactic acid than the proportion above given.

CHEESE.

§ 187. Cheese consists essentially of the coagulated albuminous matters of milk, especially of caseine, with a variable quantity of fat, common salt, and alkaline and earthy phosphates. Cheese may be made from the milk of any animal, but the great majority of cheeses in commerce are made from that of the cow. The principle of the manufacture of cheese from fresh milk is very simple: the caseine is precipitated by rennet, and carries down with it most of the milk-fat, as well as some portion of the milk-sugar. The thin whey is allowed to run off, and the precipitated "curds"* submitted to pressure, which has the effect of not only getting rid of the whey, but also of giving to the mass shape and consistency. Cheese may be made from sour milk without the addition of rennet, the lactic acid precipitating the caseine; but most of the cheeses in commerce are made from fresh milk. Cheeses may be divided into two varieties—the soft and the hard; the former are manufactured by precipitating with rennet at a low temperature, and using but little pressure; they have mostly an alkaline reaction. The hard cheeses are subjected to a higher temperature and stronger pressure, and have, when first made, an acid reaction.

I. SOFT CHEESES.

§ 188. *Neufchatel Cheese.*—This is a Swiss cream cheese; its average composition when fresh is as follows:—

	Per cent.
Water,	37·87
Caseine,	17·43
Fat,	41·30
Ash,	3·40

* An analysis of curds by M. Rubner is as follows:—

		Per cent.
Water,		60·27
Caseine,		24·84
Fat,		7·33
Ash,		4·02
Milk-sugar,		3·54
Total solids,	39·73	
"Solids not fat,"	32·40	

Fromage de Brie.—A soft French cheese, rapidly ripening and developing ammoniacal compounds :—

	Per cent.
Water,	51·87
Caseine,	18·30
Fat,	24·83
Ash,	5·00

English Cream Cheese varies within somewhat wide limits; it usually contains from 50 to 68 per cent. of fat, and from 2 to 3 per cent. of caseine.

Camembert Cheese.—This is a fine cream cheese, at present much consumed; its general composition appears to be—

	Per cent.
Water,	51·30
Caseine,	19·00
Fat,	21·50
Lactic acid, Milk-sugar, galactine,	3·50
Ash,	4·70

The Roquefort Cheese is a very celebrated French cheese, largely eaten on the Continent. It is not made from cows' milk, but from that of the ewe. A fresh Roquefort, analysed by Blondeau,* had the following composition :—

	Per cent.
Caseine,	85·43
Fat,	1·85
Lactic acid,	0·88
Water,	11·84

The same cheese, in the condition most highly prized (after it had been kept two months in a cold cellar), had the following composition :—

		Per cent.
Caseine,		43·28
Fat, Margarine,	18·30	32·30
Fat, Olein,	14·00	
Butyric acid,		0·67
Chloride of sodium,		4·45
Water,		19·30

Roquefort cheese is usually coloured with reddle or annatto. The manufacturers of these cheeses attach great importance to their being kept at a rather low and uniform temperature during

* *Annales de Chimie et de Physique*, (4) t. i., 1864.

the ripening process. The most famous cellars are subterraneous mountain-caves, kept constantly cool (at about 41° to 42° Fahr.) by currents of air coming through clefts and grottoes. The commercial value of these cellars is directly proportionate to their uniformity of temperature.

II. HARD CHEESES.

§ 189. *American Cheese* is made from unskimmed milk, and is of extremely uniform quality. The general composition of two fine-flavoured Americans, sold at 9d. per lb., the author found to be—

		(1.)		(2.)
Water,		22·59		31·80
Fat,		35·41		28·70
Caseine,		37·20		36·00
Ash, Soluble in water,	1·19	4·80	1·13	3·50
Ash, Insoluble,	3·61		2·37	
NaCl in soluble ash,		1·08		1·01
Phosphate of Lime in insoluble ash,		2·21		2·37

Cheddar Cheese is made with entire milk; the cheeses are usually thick, and weigh up to 200 lbs. each. Two sound, good-flavoured Cheddars, sold at 11d. per lb., had the following composition :—

		(1.)		(2.)
Water,		27·83		28·34
Fat,		24·04		21·01
Caseine,		44·47		47·03
Ash, Soluble in water,	1·14	3·66	1·14	3·62
Ash, Insoluble,	2·52		2·48	
NaCl in soluble ash,		1·04		1·14
Phosphate of Lime in insoluble ash,		1·52		1·69

Dunlop Cheese is made with entire milk, and is not dissimilar in general composition to American cheeses. A sample examined by Johnstone had the following composition :—

	Per cent.
Water,	38·46
Fat,	31·86
Caseine,	25·87
Ash,	3·81

Gloucester Cheese.—Two varieties of Gloucester cheese exist in commerce, single Gloucester and double Gloucester—the only difference between the two being that the latter is richer than

the former, single Gloucester being made from a mixture of skimmed and entire milk, double Gloucester from entire milk. A single Gloucester, sold at 9d. per lb., of good flavour, and free from mould, had the following composition :—

	Per cent.
Water,	21·41
Fat,	25·38
Caseine,	49·12
Ash,	4·09

An analysis by Johnstone of a double Gloucester is as follows:—

	Per cent.
Water,	35·82
Fat,	21·97
Caseine,	37·96
Ash,	4·25

Notwithstanding that in the single the fat was 25 per cent., in the double but 21 per cent., the latter is really richer than the former, if the water be subtracted, and the percentage be taken on the dry substance; or if the proportion of the fat to the caseine be considered—in the double the fat being to the caseine as 10 : 17, in the single as 10 : 19.

Parmesan Cheese.—This is a peculiar cheese, never made in this country, but imported from Parma and elsewhere. The essential points in the manufacture are, that the rennet is heated to about 46°·6 (120° Fahr.), and an hour afterwards the milk set over a slow fire until heated to about 65°·5 (150° Fahr.) These operations cause the curd to separate in hard lumps. It is usually coloured with saffron. The outer crust of the cheese at the end of fourteen days is cut off, the new surface varnished with linseed oil, and one side coloured red. It is a very dry cheese, with a large amount of caseine, and only a moderate percentage of fat. A Parmesan analysed by Payen gave—

	Per cent.
Caseine,	44·08
Fat,	15·95
Salts,	5·72
Water,	27·56
Non-nitrogenous matter, &c.,	6·69

Stilton Cheese is made from entire cows' milk, to which some cream has been added; when fully mature, it is similar in composition to Roquefort. Analyses of Stilton cheeses by Voelcker are as follows :—

	Tolerably fresh.	Old.	Not very recent.	
Water,	32·18	20·27	38·28	38·23
Caseine,	24·31	33·55	23·93	24·38
Milk-sugar,	2·22		3·70	2·76
Fat,	37·36	43·98	30·59	29·12
Ash,	3·93	2·20	3·20	5·51

Gruyère Cheese is a peculiarly-flavoured Swiss cheese. Analyses by various chemists are as follows:—

TABLE XX.—GRUYÈRE CHEESE.

	A. Payen.†	A. Payen.†	O. Lindt.†	C. Müller.†	C. Müller.*	Maximum.	Minimum.	Mean.
Water,	40·00	32·05	34·57	35·74	34·57	40·00	32·05	34·68
Caseine,	31·25	34·25	29·12	29·95	32·51	34·25	29·12	31·41
Fat,	24·00	28·40	32·51	30·64	29·12	32·51	24·00	28·93
Milk-sugar and other non-nitrogenous substances,	1·75	·51	...	...	...	1·75	·51	1·13
Ash,	3·00	4·79	3·80	3·67	3·80	4·79	3·00	3·85

Gorgonzola Cheese.—An analysis of Gorgonzola cheese, by J. Moser,‡ is as follows:—

	Per cent.
Water,	43·56
Caseine,	24·17
Fat,	27·95
Ash,	4·32

Skim Cheese.—The quality of skim cheese depends upon the amount of fat it contains. A cheese which shows under 10 per cent. of fat may with propriety be called skim, the majority of skim cheeses containing from ·5 up to 10 per cent. of fat. The writer found a sample of skim cheese, at 6d. per pound, to have the following composition:—

			Per cent.
Water,			43·14
Fat,			·86
Caseine and milk-sugar,			49·79
Ash,	Soluble in water,	2·16	6·21
	Phosphate of lime,	3·98	
	NaCl in soluble ash,	2·00	

* *Jahresbericht f. Agricult. Chemie*, 1875–6, ii. Bd.
† *Journ. de Pharmacie*, xvi.
‡ *Journal of Roy. Agricul. Soc.*, 1861, xxii.

The mean of nine analyses of skim cheese collected by König is as follows:—

	Per cent.
Water,	48·02
Fat,	8·41
Caseine,	32·65
Milk-sugar,	6·80
Ash,	4·12

The analyses given by no means exhaust the varieties of cheese. There are many others, such as Dutch cheese, usually highly salted,—English cheeses taking their name from the county or place in which they are made, and a great number of Continental cheeses.

§ 190. *The Ripening of Cheese.*—The transformation that cheese undergoes, and by which it usually acquires a more agreeable taste and flavour, is without doubt a fermentation of a slow character, induced by the agency of minute mycoderms; possibly, as F. Cohn suggests, the very active thread-bacteria, which rennet always contains, have something to do with the process. Fresh cheese has an acid reaction, but the development of ammonia ultimately renders the reaction alkaline. There is with age a continuous loss of water, and a slow development of carbond ioxide—the fat decomposes, and the fatty acids * unite in part with the lime and in part with the ammonia. The caseine also gradually passes into a soluble condition, so that a cheese, which originally gave very little to water, ultimately becomes almost wholly soluble.

Blondeau and others considered that, in the ripening of cheese, the albuminoids slowly changed into fat; thus, the Roquefort, of which two analyses are given at p. 306, was analysed at the end of a year, and its composition found to be as follows:—

	Per cent.
Caseine,	40·28
Margarine,	16·85
Olein,	1·48
Butyrate of ammonia,	5·62
Caproate of ammonia,	7·31
Caprylate of ammonia,	4·18
Caprate of ammonia,	4·21
Chloride of sodium,	4·45
Water,	15·62

Alexander Müller has, however, shown that the albuminoid and fatty constituents of old cheese bear the same relation to

* Valerianic acid has been detected in a Roquefort cheese by M. Balard, and by Messrs. J. Genko and Laskowski in a Limbourg cheese.

each other as in new cheese, which he proves by calculating the determinations according to an equal quantity of water, thus—

	Fresh.	A year old.
Water,	40·4	40·4
Caseine,	24·5	24·5
Fat,	28·0	28·2
Sugar,	1·7	2·6
Salts,	5·4	4·3

N. Sieber * has also contested the change of albuminoids into fat, and gives the following analyses of a Roquefort:—

	Fresh cheese.	After one month.	Very old cheese.
Water,	49·66	36·93	23·54
Caseine,	13·72	5·02	8·53
Soluble albuminoids,	6·93	20·77	18·47
Fat,	27·41	31·23	40·13
Ash,	1·74	4·78	6·27
	99·46	98·73	96·94

Now, although there is in the above analyses an apparent increase in the fat, yet, if reckoned on 100 parts of the dry substance, there is no very decided change. Thus—

	Fat.	Albuminoids.
Fresh cheese,	53·91	40·80
After one month,	49·94	40·53
Very old cheese,	56·14	37·78

Brassier,† some years ago, made several careful analyses, which may be of assistance in following the changes that cheese undergoes through age. Five pieces of the same cheese in the salted and unsalted condition were analysed at the end of two, four, and seven months, the results of which are tabulated in Table XXI. The development of ammonia, the production of nitrogenous products soluble in alcohol, and the wasting of the fat and total nitrogen, are well shown in these analyses.

The researches on the "ripening" of cheese hitherto made by no means exhaust the subject, and there appears room for much interesting work in this direction.

§ 191. *The Analysis of Cheese.*—The analysis of cheese when fresh is conducted on almost the same principles as the analysis of butter. The fat is best taken in a proper exhaustion apparatus, by petroleum ether, or carbon bisulphide. On extraction of the fat the fat-free solids are dried and weighed, and the fat is also dried and weighed. The dry fat and the dry solids added

* *Journ. f. Prak. Chemie*, xxi. 213.

† *Ann. de Chem. Phys.*, v.

TABLE XXI.

	Fresh cheese.	Unsalted pieces.		Salted pieces.		
		After 2 months.	After 4 months.	After 2 months.	After 4 months.	After 7 months.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
Caseine, . . .	96·21	83·10	85·01	78·60	80·10	67·06
Milk-sugar, . .	11·46	...	...	...	...	...
Leucine and other nitrogenous substances soluble in alcohol, . . .	...	21·18	18·67	15·75	18·28	33·42
Fat, ...	66·78	56·31	46·92	56·01	40·50	39·74
Insoluble salts, .	2·25	2·25	2·25	...	...	...
Ammonia, . .	....	...	...	15·53	16·75	16·50
Soluble substances, . .	Trace	1·85	1·95	1·42	1·67	3·22
Water, . . .	123·3	67·31	59·20	68·69	81·70	56·06
Total weight, .	300·0	232·0	214·0	236·0	239·0	216·0
Total nitrogen, .	15·27	15·94	12·32	13·73	14·63	10·58

together, and subtracted from the quantity taken at first, gives the amount of water. This is a better method than drying the solids in the ordinary way, which will be found in many cases to be extremely tedious and inaccurate. With alkaline cheeses there appears no other way of obtaining the amount of water than careful neutralisation of the free alkali by an acid before drying. The caseine and albumen represent the insoluble portion of the cheese. The sugar must be determined by copper oxide (see p. 119); the lactic acid and the ash on the principles laid down at pp. 244 and 98.

The *adulterations* of cheese which have actually been found are not numerous. All mineral adulterations, save those of volatile metals, must be looked for in the ash, which consists normally of common salt, alkaline, and earthy phosphates. Cheese has from the earliest to the present time been coloured by vegetable matters, and so long as the latter are not injurious, such addition cannot be considered as adulteration.

Thin slices of cheese should be examined microscopically after dissolving out the fat, &c., by ether; in this way starches and vegetable substances may be detected. Arsenical washes and lead pastes have often been applied to the rind to prevent the

attacks of the fly. As this part is habitually eaten by a few people, it is necessary to examine it, especially for these metals, and, in a complete investigation, to make two separate analyses, one of the rind, and the other of the substance of the cheese.

In past times, a few isolated instances have occurred in which it was found that the manufacturers of cheese had mixed preparations of arsenic with the cheese itself as a preservative:—*e.g.*, such was the case in the year 1841, when several of the inhabitants of Chatillon were poisoned by this means. In 1854, the same thing occurred, and a Parisian family suffered, but not fatally (*Chevallier*). It is to be hoped that such ignorance is a thing entirely of the past.*

BIBLIOGRAPHY.

BLONDEAU.—*Annales de Chim. et de Physique*, (4), i., 1864.
BLYTH, A. WYNTER.—Art. Cheese, "Dicty. of Hygiène."
BRASSIER.—*Ann. de Chim. Phys.*, v. 270; *Chem. Centr. Bl.*, 1865.
COHN, F.—*Dingl. Polyt. J.*, ccxx. 191; *Journal of Chem. Society*, ii., 1877, 342.
KELLNER, O.—*Landwirthsch. Versuch*, 26, s. 39.
MÜLLER, A.—*Landw. Jahrbücher*, 1872.
MUSPRATT'S "Chemical Dictionary," Art. Cheese.
STORCH, V.—*Bied. Centrbl.*, 1880, 366-370.
SIEBER, N.—"Ueber die angebliche Umwandlung des Eiweiss im Fett beim Reifen des Roquefort Käse." *Journ. f. Prak. Chem.*, xxi. 213.

* *Whey.*—After the removal of the curd from milk, a "whey" remains, containing albumen, galactine, milk-sugar, lactic acid, and salts. The mean of thirty-two analyses collected by König gives the following as the average composition of "whey":—

Water,	93·31
Nitrogenous substances,	·82
Fat,	·24
Milk-sugar,	4·65
Lactic acid,	·33
Salts,	·65

Whey, on account of its high content of milk-sugar, is used for the preparation of the latter, and there is also a "whey-vinegar." In very many places, however, whey is used merely as a food for pigs.

PART V.—TEA, COFFEE, COCOA.

TEA.

§ 192. *Varieties of Tea.*—Tea is the dried leaf of different species of *Thea*, a section of the genus *Camellia*. The botanical varieties do not appear to be numerous. *Thea Bohea*, *T. viridis*, and *T. sinensis*, all Chinese plants, *Thea Assamica*, indigenous to Assam, and one or two hybrids, are the principal plants from which the numerous teas of commerce are derived. The difference depends on the selection of young or old leaves, and special treatments in drying and otherwise preparing the leaf, rather than on essential botanical variation.

The varieties of tea imported into this country are extremely numerous; but seldom does any one of them reach the consumer unmixed, for the wholesale tea merchants carefully improve their teas by "blending." The most common sorts are—Gunpowder, Hyson, Congou, Capers, and Indian tea. Of these, the Gunpowder and Hyson are dried at a higher temperature than the others, and contain less hygroscopic moisture. The Capers may be generally told by the leaves being rolled up into little lumps with starch or gum; as a class, they are much adulterated, and, in fact, can hardly be called genuine tea.

Besides these, there are a number of special teas, some of a very high price, and imported in a state of great purity; but such teas are used almost entirely for mixing or blending.* They are known under the names of Moyone, Moyone gunpowder,

* In Cooper's travels ("Travels of a Pioneer of Commerce," by T. T. Cooper, London 1871), there is an interesting account of the brick tea used in Thibet, some of which may find its way to Russia, but none, probably, to this country. It is the staple produce of the city and district of Yatzow, and the tree from which it is prepared attains not unfrequently the height of 15 feet. It has a large coarse leaf, and is cultivated with little care, growing along the borders of fields and homesteads. There are three qualities of the tea: the first is gathered in June and July, when the leaf is about an inch long. It is spread out in the sun to dry slightly, then rolled in the hand until the sap begins to exude, and when in this state made up into balls, and laid on one side to ferment. After fermentation, it is pressed into wooden moulds, and dried by charcoal fires. The bricks on their removal from the moulds are enveloped in yellow paper covers, bearing a Government stamp and the trade mark of the exporter, and then they are packed in baskets four feet long, made of the thin strips of the bamboo.

Oolong, Mannuna Kaisow, scented Pekoes, Indian Souchong, Assam, Java, &c. The names by which the teas of commerce are most familiar to the public are simply "green" and "black," which differ merely in accordance with the method of preparation followed. Green tea is prepared from young leaves, which are roasted over a wood fire within a hour or two after being gathered. The black tea leaves, on the other hand, are allowed to lie in heaps for ten or twelve hours after they have been plucked, during which time they undergo a sort of fermentation; the leaves then pass through certain processes, and are slowly dried over charcoal fires.

§ 193. *Structure of the Tea Leaf.*—The border is serrated nearly, though not quite, up to the stalk (see fig. 28). The primary veins run out from the midrib almost to the border, and then turn in, so that a distinct space is left between them and the border. The diagnostic mark of a tea leaf is, however, the microscopic appearance of its epidermis, which, especially that of the lower side (see fig. 29), exhibits numerous small stomata formed of two reniform cells of an average length of ·00075 inch, and average breadth ·000588 inch. Around the stomata are seen elongated and curved epidermic cells. This appearance, so far as is known, is met with only in the tea plant. Stomata are infrequent on the upper surface, the epidermal hairs are simple.

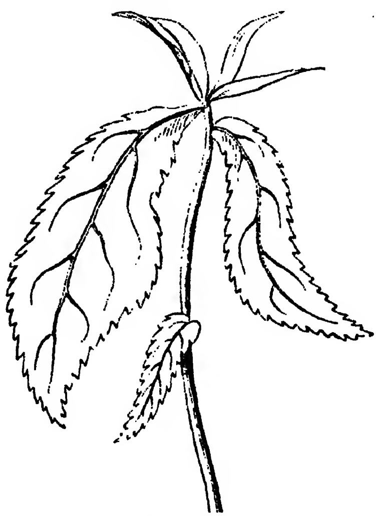

Fig. 28. TEA PLANT

§ 194. *Chemical Composition of Tea.*—The constituents of tea are—*Essential oil, theine, boheic acid, quercetin, tannin, quercitrinic acid, gallic acid, oxalic acid, gum, chlorophyll, resin, wax, albuminous, woody, and colouring matters, and ash.* The essential oil of tea

The bricks thus packed form a "packet of tea," and weigh about 20 lbs.; at Llássa, this quality of tea sells for 4s. 8d. per lb. The second variety consists of the older and yellower leaves which, when exported to Lethang and Bithang, sell for 1s. 6d. per lb. The third variety is merely chopped twigs stuck together by rice water, and is only used in the neighbourhood of Ta-tsian-too, where it is sold at 9d. per lb.

varies from 0·6 to 1 per cent. It is citron-yellow, lighter than water, has a strong odour of the tea plant, solidifies easily by cold, and resinifies on exposure to air.*

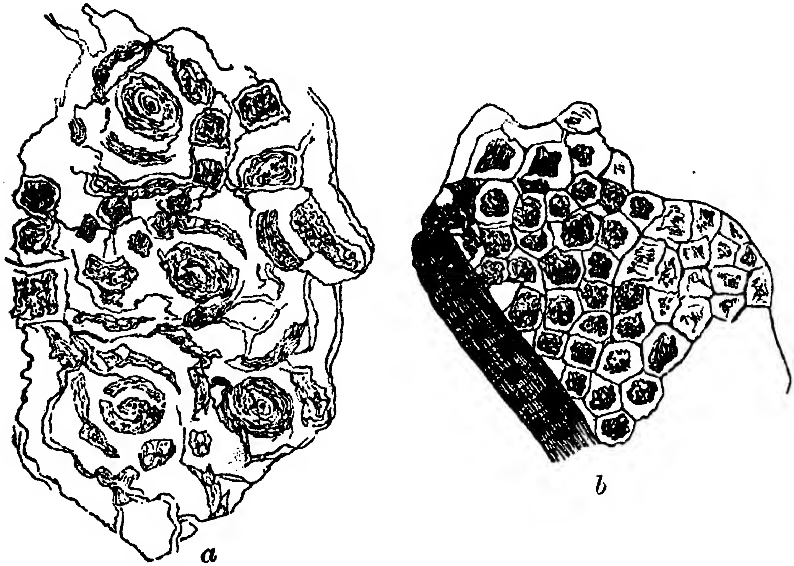

Fig. 29.—EPIDERMIS OF TEA LEAF, × 300. *a* under, *b* upper surface.

Theine, Caffeine, $C_8H_{10}N_4O_2$.—This alkaloid was first separated in an impure condition by Runge, from coffee berries, in the year 1820. It was found by Corput and Stenhouse also to be a constituent of the leaves of the coffee tree. Oudry in 1827, finding it in various species of tea, named it "Theine," and Oudry's "Theine" Mulder and Jobst showed, in 1838, to be identical with caffeine. The alkaloid has also been discovered in guarana, maté, and the kola nut, by Martius, Stenhouse, and Attfield respectively.

Theine crystallises from an aqueous solution with 1 atom of water; from ether, in an anhydrous state. It sublimes in minute dots at 78°·8, in crystals at 79°·4 (175° Fahr.), and above.† The

* A fixed oil, serving many purposes in China, is extracted from the seeds of the tea plant. It is citron-yellow, specific gravity 0·927, and is composed of one part of stearin and one of olein.

† The subliming point given by Pelouse, 178°, and by Mulder, 184°·7, must have been obtained by extremely faulty methods. If a little theine is placed between two watch-glasses on the water-bath, the almost instantaneous rise of crystals to the upper glass will at all events show that the subliming point is below 100°. See the author's paper, "Temperature at which the Alkaloids Sublime," *Journal of Chemical Society*, 1878.

sublimate consists of microscopic needles: that which is first produced is of extremely fine, light elements; after a little time, at such temperatures as 120°, the crystals become longer and larger. The melting point of theine is somewhere between 177° and 228°. Theine possesses a slightly bitter taste, but is without odour. According to a recent research, the solubility of theine in different solvents is as shown in the table below.

Theine forms numerous salts of definite composition—the hydrochlorates, $C_8H_{10}N_4O_2$, HCl and $C_8H_{10}N_4O_2$, 2HCl; a platinum compound, $C_8H_{10}N_4O_2$, HCl, $PtCl_2$; a chloride of gold compound, $C_8H_{10}N_4O_2$, HCl, $AuCl_3$; a chloride of mercury compound, $C_8H_{10}N_4O_2$, 2HgCl; an argentic nitrate compound, $C_8H_{10}N_4O_2$, $AgNO_3$, and many others. Some of these, such as the silver compound, separated from a concentrated watery solution, and the mercury compound, almost insoluble in ether, and capable of being dried at 100°, might possibly be of use in the estimation of theine.

Theine is, in large doses, a poison. Frerichs, C. J. Lehmann, Husemann, and others, have made themselves the subject of experiment. Lehmann, after taking ·5 grm., suffered from frequency of the pulse, irritation of the bladder, cerebral excite-

TABLE XXII.—SOLUBILITY OF THEINE.

	100 grms. of Solvent at 15° to 17° dissolved of Theine.		Co-efficient of Solubility at 15° to 17°.		100 grms. of Solvent at the boiling point dissolved of Theine.		Co-efficient of Solubility at the boiling point.	
	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.	Hydrated.	Anhydrous.
Chloroform,	...	12·97	...	1/7·72	...	19·02	...	1/5·25
Alcohol of 85 per cent.,	2·51	2·30	1·40	1/44·4	...	...	...	...
Water,	1·47	1·35	1·68	1/74·2	49·73	45·55	1/2·01	1/2·19
Absolute Alcohol,	...	0·61	...	1/164·7	...	3·12	...	1/32
Commercial Ether,	0·21	0·19	1/476	1/526	...	0·454	...	1/220
Carbon Bisulphide,	...	0·0585	...	1/1709	...	...	...	...
Purified Anhydrous Ether,	...	0·0437	...	1/2288	...	0·36	...	1/277
Light Petroleum,	...	0·025	...	1/4000	...	...	...	...

ment, slight hallucinations, and lastly desire to sleep. Husemann took ·25 grm. with somewhat similar symptoms. Pratt, with subcutaneous injections of from ·12 to ·8 grm., suffered from symptoms rather different from the foregoing; ·3 grm. lessened the pulse and caused sleeplessness; ·4 to ·5 grm. quickened the pulse, and caused a desire for frequent micturition, but no dilation of the pupil; ·8 grm. caused great uneasiness and anxiety, trembling of the hands and arms, so that he was unable to write, and later a restless sleep, with continual dreaming. In opposition again to all these statements, is that of the late Mr. Cooley,* who is said to have taken 20 grains (1·29 grm.) of pure theine every day for a month without experiencing any other symptom than some slight elevation of spirits. According to Strauch, the least fatal dose for cats is ·25 grm., a quantity which killed a cat in 35 minutes. In all experiments on animals there has been increased frequency of the heart's action, and repeated emptying of the bladder and intestine. No case of poisoning in the human subject appears to be on record. When given to animals it has been chemically separated from the blood, urine, and bile.

Tests for Theine.—Concentrated sulphuric and nitric acids dissolve theine in the cold without the production of colour. If the alkaloid is treated with fuming nitric acid, and evaporated to dryness, the reddish-yellow residue becomes, when moistened with ammonia, of a splendid purple-red colour. If a solution of theine be evaporated with chlorine water in a watch-glass, a red-brown residue is obtained, which on cooling, and exposure to the vapour of strong ammonia, becomes purple-violet. The chief precipitants of theine are—phospho-molybdic acid, yellow precipitate; iodine with potassic iodide, dirty brown precipitate; chloride of platinum, yellow hair-like crystals, insoluble in cold hydrochloric acid, slowly separating; chlorides of gold, mercury, and nitrate of silver also give precipitates.

Boheic Acid, $C_7H_{10}O_6$, was first separated by Rochleder in 1847,† from the leaves of *Thea sinensis*. The hot watery decoction of tea is precipitated whilst boiling by sugar of lead, filtered, the filtrate neutralised by ammonia, the resulting precipitate collected, suspended in absolute alcohol, and freed from lead by SH_2; the filtrate from the lead precipitate is evaporated to dryness in a vacuum, and purified by re-solution in water, &c. It is a pale yellow amorphous powder, melting at 100° into a tenacious mass, and decomposing at common temperatures if exposed to the air. It is soluble in all proportions in water and

* *Vide* Cooley's "Dictionary of Practical Receipts," Art. Caffeine.
† Rochleder: *Ann. Chem. Pharm.*, lxiii. 202.

alcohol, is coloured brown (but not precipitated) by chloride of iron, and forms for the most part amorphous salts insoluble in water.

Quercitrinic Acid, $C_{33}H_{30}O_{17}$, first discovered by Chevreul and Brandt in the *Quercus tinctoria*, and stated by Hlasiwetz to be in tea leaves, can be crystallised from an aqueous solution. It forms sulphur or chrome-yellow microscopic tables, containing 3 atoms of water, part of which is expelled at 100°, the rest at from 165° to 200°. Its reaction is neutral, and it is without odour, but has a marked bitter taste when in solution. It melts at from 160° to 200° to a resinous, amorphous mass. Its solubility is as follows:—Cold water 2485, boiling 143; cold absolute alcohol 23·3, boiling 3·9; ether dissolves it slightly, warm acetic acid copiously. Sugar of lead precipitates almost completely; the precipitate is soluble in acetic acid.

Quercetin, first obtained by Rigaud, 1854, from the splitting up of quercitrinic acid is, according to Filhol, to be found in the green leaves and flowers of all plants. Its formula is given as $C_{20}H_{18}O_{12}$; it forms fine yellow needles, or a citron-yellow powder, which gives up at a temperature of 120°, 7 to 10 per cent. of water of crystallisation. It melts, according to Zwenger and Dronke, above 250° without decomposition, solidifying again in a crystalline mass, and it may be also sublimed with only partial carbonisation. It is very little soluble in water. Warm acetic acid dissolves it copiously, but it separates on cooling. It is soluble in 229·2 parts of cold, and 18·2 parts of hot absolute alcohol. A solution of quercetin colours linen bright yellow; sugar of lead precipitates the alcoholic solution cherry red, and chloride of iron dark red. A combination with sodium or potassium can be obtained, $Na_2O,C_{27}H_{18}O_{12}$.

The other constituents of tea, such as gallic and tannic acids, gum, &c., are too well known to need description.

ANALYSIS OF TEA.

§ 195. We possess no complete analysis of tea; partial analyses are numerous. An often quoted one by Mulder is as follows:—

	Black Tea.	Green Tea.
Essential Oil,	0·60	0·79
Chlorophyll,	1·84	2·22
Wax,	0·00	0·28
Resin,	3·64	2·22
Gum,	7·28	8·56

	Black Tea.	Green Tea.
Tannin,	12·88	17·80
Theine,	0·46	0·43
Extractive Matter,	21·36	22·80
Colouring Substances,	19·19	23·60
Albumen,	2·80	3·00
Fibre,	28·33	17·80
Ash (Mineral Substances),	5·24	5·56

The theine here is certainly too low, but the amounts of the other constituents are a tolerably just representation of what may be usually found. Some partial analyses recently published by Dragendorff may be reproduced here, as probably the only extended and trustworthy researches on the amount of theine, the alkaloid having been extracted by a fairly reliable method. *(See annexed table.)*

The time is probably not far distant when the tea trade will buy entirely by analysis, supplemented in a few cases by a "taster's" report. An experienced palate will detect particular flavours which analysis may fail to show; but a fairly complete chemical examination of tea is of the highest value, whether as a guide to the purchaser, or merely to show its freedom from adulteration.

Preliminary Examination of Tea.—The tea leaves should be soaked in hot water, carefully unrolled, and their shape and structure examined. Sections of leaves can be made by placing them between two pieces of cork, and cutting fine slices off both the cork and the enclosed leaf; on floating the sections in water, the film of cork may be readily separated from the leaf. The epidermis of the lower or upper surface can, with a little practice, be detached in small portions by the aid of a sharp razor, and examined in water, glycerine, or dammar balsam, under the microscope. Its structure has been already detailed.

§ 196. *New Process for the Examination of Leaves and Vegetable Tissues generally under the Microscope.*—The author has recently discovered a very easy process for examining vegetable leaves. A portion of a leaf is enclosed between two of the thin circles of glass used by all microscopists, and a weight having been placed upon the upper glass, the portion of leaf thus enclosed is heated with a strongly alkaline solution of permanganate of potash. The action begins at once, and the substance under examination must be examined from time to time to see that the oxidisation does not proceed too far. Alkaline permanganate attacks the colouring-matters, the contents of the cells first, and afterwards the cell membranes; the object of this treatment is to make the leaf transparent, and yet to preserve its structure. Tea leaves are very opaque, and it is impossible without some mechanical or

chemical treatment to render them transparent. When from the appearance of the leaf-fragment the oxidation is considered sufficient, it is removed, washed in water, and treated with a little strong hydrochloric acid, which at once dissolves the manganese oxide that has been precipitated on the leaf, and leaves the latter as a translucent white membrane, in which the details of structure can be readily made out—tea-leaf in this way being quite different in appearance from other leaves. A second method of very great value is to place a fragment of a leaf between two circles* of glass, weight the upper one with a silver coin, and burn on a bit of sheet platinum the leaf thus prepared. Since it is impossible for the ash to curl up and become disarranged, a complete skeleton of siliceous ash remains, which may be called "*the skeleton ash.*"

Fig. 30.—Ash of Tea Leaf, × 170.

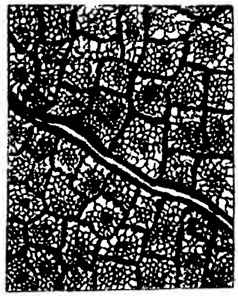

Fig. 31.—Ash of Sloe Leaf, × 29.

Fig. 32.—Ash of Lime, × 29.

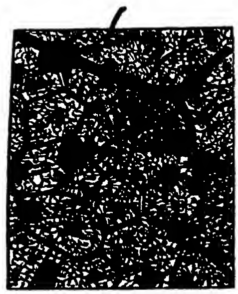

Fig. 33.—Ash of Tobacco Leaf (Cigar), × 29.

These skeleton ashes of leaves (so far as the author has hitherto been able to investigate the subject), show such decided differences the one from the other, that a great number of leaves may with a little practice be recognised by this

* That is, the covers of thin glass used by the microscopist.

method alone. [It is particularly useful in detecting the adulterations of tobacco, the skeleton-ash of the tobacco-leaf being special and peculiar.] It is sometimes well not to burn to an absolute ash, but to leave little bits of partially consumed carbon, forming objects for the microscope of great beauty. To preserve the "skeleton-ash" the two circles may be cemented together, or the edges may be fused by the flame.

Figs. 30, 31, 32, and 33 are examples of *skeleton ashes*, as drawn on the block to scale.

§ 197. *Chemical Method for the Detection of Foreign Leaves in Tea.*—A chemical method for the detection of foreign leaves (adulterants) was first described by the writer in June, 1877.* It is based upon two facts—firstly, that every part of a *theine*-producing plant—wood, stem, leaf, flowers, and even hairs—contains the alkaloid; and, secondly, that this can be readily sublimed. The leaf, or fragment of a leaf, is boiled for a minute in a watch-glass with a very little water, a portion of burnt magnesia equal in bulk is added, and the whole heated to boiling, and rapidly evaporated down to a large-sized drop. This drop is transferred to the "subliming cell," described in the second volume of this work, and if no crystalline sublimate be obtained, when heated up to 110° (a temperature far above the subliming point of theine), the fragment cannot be that of a tea plant. On the other hand, if a sublimate of theine be obtained, it is not conclusive evidence of the presence of a tea leaf, since other plants of the camellia tribe contain the alkaloid.

Finally, there is a negative test which may occasionally be valuable. All fragments of tea hitherto examined contain manganese, and there are a few foreign leaves in which manganese is constantly absent. Hence, if a leaf be burnt to an ash, and a fragment of the ash be taken up on a soda-bead, to which a little potassic nitrate has been added, the absence of the green manganate of soda would be sufficient evidence that the leaf had not been derived from the tea plant, while conversely, as in the case of theine, it does not in itself prove it to be tea.

Another portion of the tea leaves should be thoroughly bruised, spread on a glass plate, and carefully searched with a magnet for ferruginous particles—the so-called iron-filings, which are occasionally found, especially in Capers and certain species of Congou. It is almost unnecessary to state that the black, irregular masses found in tea, and attracted by a magnet, are not metallic iron.†

* Micro-Chemistry as applied to the identification of tea leaves. *Analyst*, 1871.

† Mr. Allen appears to have found metallic iron in tea. The test for

Their chemical composition is somewhat variable; they all contain magnetic oxide of iron, and many of them in addition phosphate of iron, titanate of iron, quartz, and mica, with a little sand. They are, without doubt, sometimes an adulteration (the author has himself found over 1 per cent.), and sometimes an impurity, for in a few teas mere traces only of this ferruginous sand may be discovered. Any particles of the kind extracted by the magnet should be collected and treated with hot water, which soon disintegrates them; the adherent tea-dust is separated, and the sand dried and weighed.

To detect facing, the tea in its dried state should be mounted as an opaque object.* If it has the appearance of being heavily faced, soaking in warm water will soon detach the film; and indigo, Prussian blue, or similar substances will sink to the bottom, and may be collected and examined. Indigo may be identified by the microscope. Prussian blue may be tested for by warming the deposit with caustic alkali, filtering, acidifying the filtrate with hydrochloric acid, filtering again if necessary, and testing the filtrate with ferric chloride. The residue left after treatment with caustic alkali may be tested for magnesium silicate, by first extracting with HCl, and then collecting the insoluble residue, and fusing it with an alkaline carbonate. The silica is now separated in the usual way by evaporation with HCl to dryness, subsequent solution in weak acid, and filtration; any lime is removed by ammonia and ammonic oxalate; and lastly, magnesia is precipitated as ammon. mag. phosphate. Magnesia found under these circumstances must have been present as steatite or other magnesian silicate.

metallic iron is, that nitric acid, 1·2 specific gravity, dissolves it with the production of red fumes; it also precipitates metallic copper, if added to an acidulated solution of cupric sulphate.

* The facing of tea is thus described by M. S. Julien: "The leaves are mixed either with powdered indigo, with powdered plaster, or with slaked lime, sometimes even all three substances being put together in small proportion to tea leaves. These matters are introduced into the basins at the commencement of the operation, when the leaves begin to be covered with a light dew under the influence of heat. These matters attach themselves to the leaves, and communicate to them the bluish-green characteristic of green tea. . . . In certain manufactories Prussian blue is used instead of indigo." "Industries Anciennes et Modernes de l'Empire Chinois," par MM. Stanislaux Julien et O. Champion. Paris, 1869.

LEAVES USED, OR SUPPOSED TO BE USED, AS ADULTERANTS.

§ 198. The following is a brief description of the principal leaves supposed to be used as adulterants :—

Beech (*Fagus sylvatica*).—The leaves of the beech are ovate, glabrous, obscurely dentate, ciliate at the edges, the veins running parallel to one another right to the edge. The leaf, slightly magnified, is seen to be divided into quadrilateral spaces by a network of transparent cells. On section, the parenchyma of the leaf is found to consist of an upper layer of longitudinal cells, and a lower of loose cellular tissue, enclosed between the epidermis of the upper and under surface. The whole section is thus divided into oblong spaces by transparent cells connecting the cuticle of the upper and lower surfaces. The epidermis of both the upper and lower surfaces is composed of cells with an extremely sinuous outline (see fig. 34). The stomata are small, not numerous, and almost round. Beech leaves contain manganese.

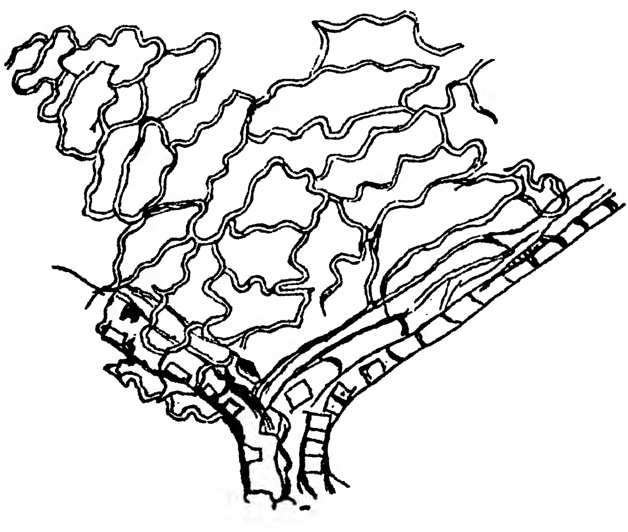

Fig. 34.—Epidermis of Beech Leaf, × 300.

Hawthorn (*Cratægus oxyacantha*).—At least two varieties, the more common of which is the *C. monogyna*, with obovate three- to four-deeply lobed leaves, with the lobes acute. The leaf is

divided into quadrilateral spaces, like the beech and many other leaves, by a transparent network. The epidermis of the upper surface is composed of a layer of thin-walled cells, generally quadrilateral, outline seldom sinuous. The epidermis of the lower surface has a layer of thin-walled cells, with a very sinuous outline. Stomata large, distinct, and numerous, in many instances nearly round, but the shape mostly oval. (See fig. 35.)

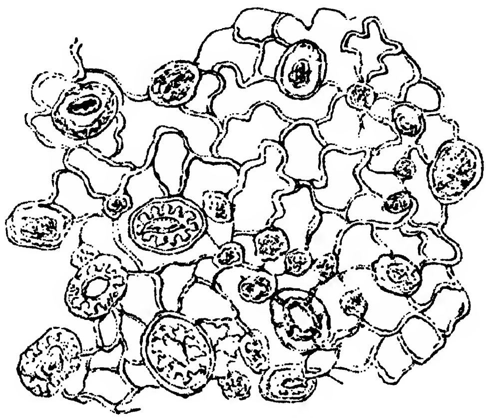

Fig. 35.—Epidermis from the Under Surface of the Hawthorn Leaf, × 300.

Camellia Sassanqua.—The leaves of *Camellia sassanqua* are oval, obscurely serrate (the younger leaves entire), dark green, glabrous, of somewhat leathery consistence; the lateral veins of the leaf are inconspicuous.

Micro-structure.—The parenchyma of the leaf is placed between two thickened epidermal layers; the epidermis of the upper surface, as seen upon a section, forms a wrinkled, continuous, thick membrane, in which a cellular structure is not very evident. Below this there are two or three layers of large cells, more or less oblong, with their long diameter at right angles to the surface of the leaf; and underneath this again is a loose network of cells, resting upon an epidermis in every respect similar to that of the upper surface, but only half as thick. A thin layer of either the upper or lower epidermis shows a peculiar dotted or reticulated appearance, not unlike the rugæ of a stomach. The lower epidermis is studded with frequent stomata, small, and of an oblong shape (see fig. 36).

Sloe (Prunus communis).—The leaves of the common sloe are

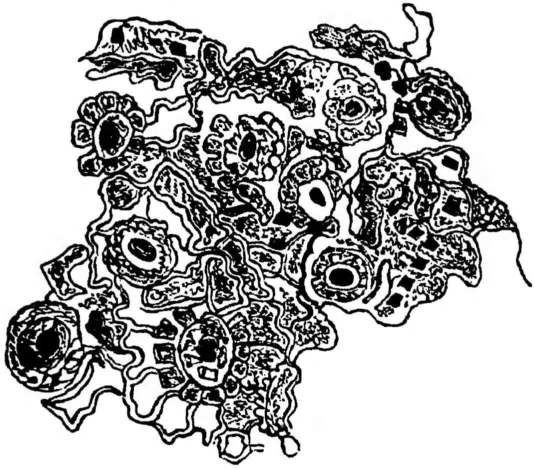

Fig. 36.—EPIDERMIS OF UNDER SURFACE OF THE LEAF OF THE CAMELLIA SASSANQUA, × 300.

rather small, elliptic or ovate-lanceolate in shape, and slightly downy beneath. The sectional thickness of the leaf is the same

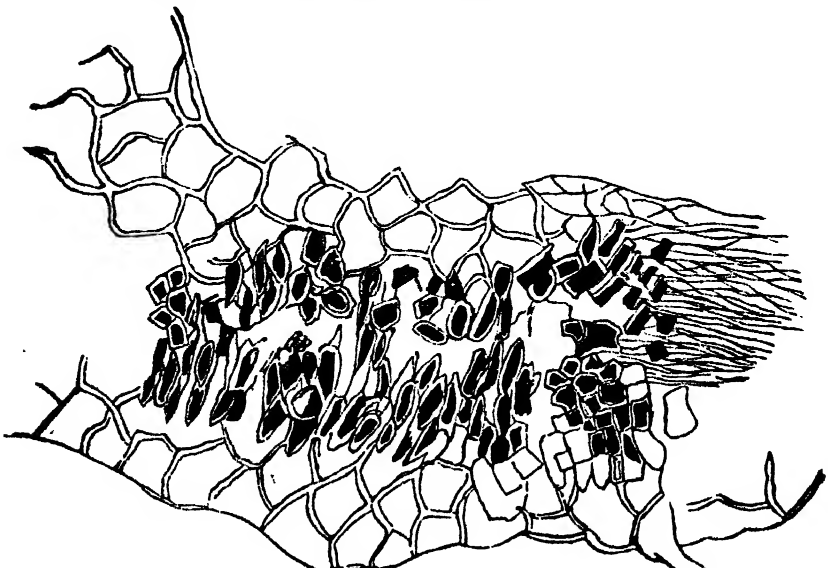

Fig. 37.—SECTION OF SLOE LEAF, × 300.

as that of tea. The stomata on the lower surface are scanty. The microscopical appearances are wholly different from those of tea leaves, more especially as seen in section. (See fig. 37.)

Chloranthus Inconspicuus.—The leaves of the *Chloranthus inconspicuus* are long, oval, serrate, wrinkled, the veins running nearly to the edge, and there forming a network in such a manner, that at the point of intersection little knots are formed, which

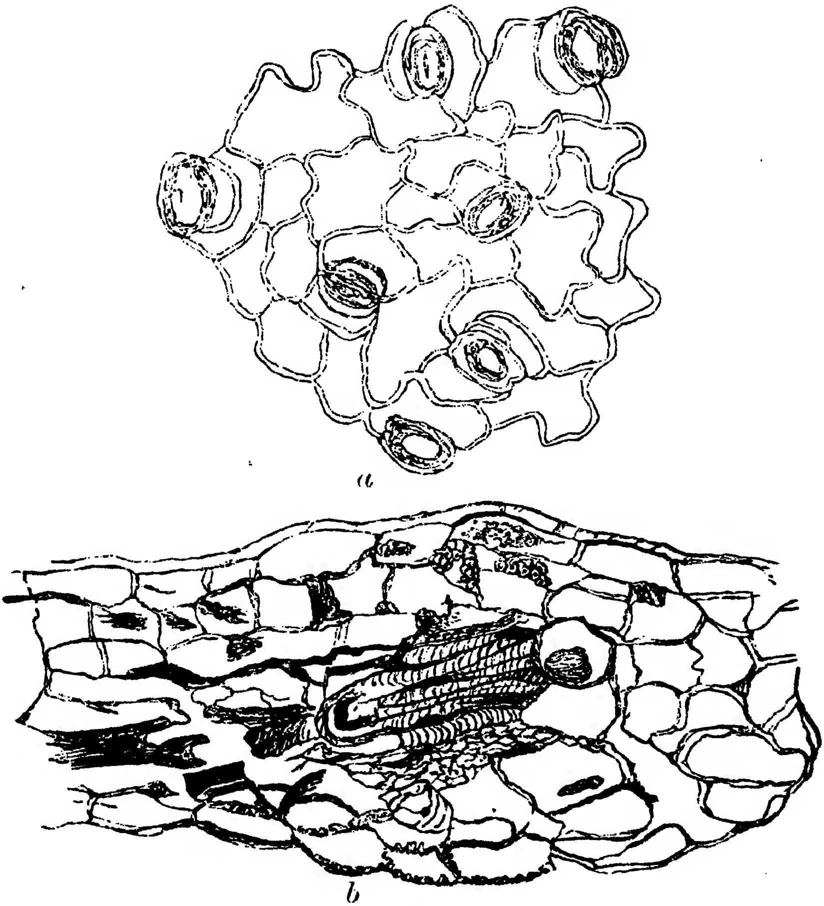

Fig. 38.—(*a*) Epidermis of Under Surface of the Leaf of Chloranthus Inconspicuus, × 300.
(*b*) Section near Edge.

give the margin of the leaf a very rough feeling. The structure of the leaf is very simple. The epidermis of the upper surface is formed of one or two layers of thin-walled cells, the epidermis of the lower of one or two layers also of cells, and between the two there is a parenchyma of loose cellular tissue. The stomata are oval and rather numerous; their length is from ·0010 inch, their breadth ·00073 inch. The cells of the epidermis are large, some of them ·005 inch or more in their long diameter.* (See fig. 38.)

§ 199. *Chemical Analysis.*—The preliminary examination of the tea having been concluded, the sample is next submitted to chemical analysis. If the question to be decided is simply that of adulteration, the taste of the infusion, the percentage of extract, and a determination of the chief constituents of the ash are in most cases all that is necessary; but a more or less complete examination embraces a quantitative estimation of hygroscopic moisture, theine, total nitrogen, tannin, extract, gum, and ash.

§ 200 *Hygroscopic Moisture.*—The ordinary method of taking the hygroscopic moisture of tea is to powder as finely as possible an indeterminate quantity of from 1 to 2 grms., and to heat it in a watch-glass over the water-bath until it ceases to lose weight. It should be finally weighed between two watch-glasses, since it rapidly absorbs moisture from the air.

The method given is in its results incorrect, since some volatile oil and a small proportion of theine are always volatilised. That theine is actually lost is capable of rigid demonstration; it is only necessary to heat a few leaves of tea between two watch-glasses over the water-bath, and theine crystals can be readily discovered by the microscope. To devise a process of drying tea which will represent water only is easy; but since the loss both of volatile principles and theine does not materially affect the results, it is scarcely worth while to complicate the analysis by the use either of a lower temperature or of processes of absorption. The highest amounts of moisture in a genuine tea which are on record are two specimens from Cachar, analysed by Professor Hodges—the one (indigenous) gave 16·06 per cent., the other, a hybrid, 16·2 per cent. These were, however, not commercial teas, and appear to have been simply dried in heated rooms. The average hygroscopic moisture found by Mr. Wigner

* The leaves of *Epilobium angustifolium* (*common willow herb*) are said to be extensively used in Russia for the adulteration of tea. The dried leaves are sold for from four to six roubles a pound, and are used by the poorer classes in the place of tea. Alcohol produces in infusions of epilobium a precipitate of mucilage.—*Pharm. Zeitsch. für Russland* and *Year-Book of Pharmacy*, 1876.

in thirty-five teas, consisting of Hysons, Capers, Souchongs, Gunpowders, and others, was 7·67 per cent., the driest teas being the Hysons and Gunpowders, the moistest the Congous :—

				Per cent.
The maximum amount of moisture found in Hyson,			.	5·68
The minimum	,,	,,	,, .	4·84
The maximum	,,	,,	Gunpowder,	6·55
The minimum	,,	,,	,,	4·94
The maximum	,,	,,	Congou, .	10·33
The minimum	,,	,,	,, .	6·36

§ 201. *The Estimation of Theine or Caffeine.*—The modern processes for extracting theine fall chiefly under three heads :—

(1.) *Extraction by treating a decoction of the theine-containing substances with lime or burnt magnesia, evaporation to dryness, and subsequent solution of the alkaloid by chloroform, ether,* or *benzine.*—The fundamental idea of this process, perhaps, belongs to Müller; it has also, with various modifications, been recommended by Clous, Commaille, Dragendorff, and many other chemists.

Commaille adopts the following method :—5 grms. of the finely powdered and carefully sifted substance are made into a hard paste with 1 grm. of calcined magnesia. This, after standing for twenty-four hours, is dried upon a water-bath and powdered. The resulting green powder is exhausted three successive times in a flask with boiling chloroform, the flask being connected with an inverted Liebig's condenser, so that the action may be continued for a long time. The cool solution is filtered, the chloroform recovered by distillation, and the residue in the flask dried. This residue consists of resinous fatty matters and theine; the former are removed by treating the contents of the flask with hot water and 10 grains of powdered glass, which have been previously washed with dilute hydrochloric acid. The water is boiled and the contents shaken up with the glass; the resinous matters attach themselves to the latter in the form of little globules. The solution is poured on a wet filter, and the residue completely exhausted by repeated boiling with fresh quantities of water. On evaporating the united filtrates in a tared capsule, pure caffeine is left in the form of white crystals.

Dragendorff takes 5 grms. of the substance, exhausts it with boiling water, evaporates to dryness, adding 2 grms. of burnt magnesia and 5 of ground glass; the finely powdered residue is soaked in 60 cc. of ether for twenty-four hours, and finally thoroughly exhausted by ether. The latter, when separated and evaporated, leaves the theine in a tolerably pure state. He also states that ether may be replaced by chloroform. Cazeneuve and Caillot recommend a very similar process, but magnesia is

replaced by recently slaked lime,* ether by chloroform. Markownikoff uses benzine instead of the solvents mentioned.

In all the above processes there is one source of error which does not appear sufficiently guarded against—viz., loss of theine during the evaporation to dryness, since it is absolutely impossible to evaporate a decoction of tea and magnesia to dryness at 100° without loss of the alkaloid—a loss which, so far as the author's experiments go, does not take place until the mixture is quite dry. The following modification may therefore be proposed :—4 to 5 grms. of the tea are boiled in a flask provided with an inverted Liebig's condenser for a couple of hours, the liquid and leaves are transferred to an evaporating dish, some magnesia added, and the whole concentrated to a pasty condition. This paste is treated and thoroughly exhausted by chloroform ; the latter is separated and evaporated, and the chloroformic extract redissolved in a little boiling water, the solution filtered, evaporated to dryness at a very gentle heat, and weighed.

(2.) *Simple Treatment of the powdered Leaves by Solvents.*—Legrif and Petit soften the leaves first with boiling water, and then extract the moist mass by the aid of chloroform. Other chemists simply exhaust the powdered substance by chloroform or ether; subsequent purification may, of course, be necessary.

(3.) *Sublimation.*—A method of utilising tea dust by making it a source of theine, was recommended by Heijnsius (*Journ. Prac. Chem.*, xlix. 317). The tea dust was simply treated in a Mohr's benzoic acid subliming apparatus. Stenhouse improved this process by precipitating either a spirituous extract, or a decoction of tea by acetate of lead, evaporating the filtrate to dryness, mixing the residue with sand, and subliming. These processes of sublimation, however, were proposed simply for the extraction, not the estimation, of theine.

The writer, in 1877,† proposed the following quantitative method of sublimation :—A convenient quantity of the tea was boiled in the way mentioned, magnesia added, and the whole evaporated to a paste, which was spread on a thin iron plate, and covered with a tared glass funnel. The heat at first was very gentle, but was ultimately raised at the later stages of the process to 200°. The theine sublimes perfectly pure and anhydrous, and forms a coherent white coating on the sides of the funnel; the increase of weight is simply anhydrous theine. To ensure success it is absolutely necessary—

(1.) That the layer be as thin as possible.

* The present writer does not believe that magnesia can be replaced with lime without loss of theine from decomposition.

† *Op. cit.*

(2.) That the heat be only gradually increased.
(3.) That the mixture be occasionally cooled, and then thoroughly stirred.
(4.) That the sublimation be prolonged for a sufficient time.

The sublimation is finished when a funnel, inverted over the substance, heated to about 150°, and left for half an hour, shows no crystals.

An improvement on this process is to place the paste on a ground glass plate, to which a flanged funnel has been ground so as to fit air-tight. The apparatus is then connected with a Lane-Fox mercury-pump, and an absolute vacuum produced. By the aid of a shallow sand-bath, the theine may be sublimed at a very gentle heat.

§ 202. *Determination of Total Nitrogen.*—Peligot, and Wanklyn as well, has laid particular stress on the large amount of nitrogen contained in tea leaves. This nitrogen is, of course, largely dependent on the theine, and it is questionable whether, with the improved methods for the extraction of the latter, it is worth while to make a combustion, more especially as the exhausted leaves are highly nitrogenous, from the presence of an albuminous body. The process is conducted in the usual way in a combustion tube, and best with copper oxide. The following are a few determinations of total nitrogen :—

	Per cent.	Analysed by
A sample of genuine tea from Cachar, .	4·74	*Hodges.*
A hybrid variety, do., .	2·81	,,
Another sample from Cachar, . . .	4·42	,,
Sample taken from 60 green teas slightly faced, ...	3·76	,,
60 Black teas, ...	3·26	*Wigner.*
6 Assam teas, ...	3·64	,,
6 Caper teas, ...	3·32	,,
Assam tea, from Dr. M'Namara's garden,	3·88	,,
Sample of exhausted leaves, ...	3·80	,,

Mr. Wanklyn has applied his ammonia process to the examination of tea. The soluble matter from 100 mgrms. of tea is heated with a 10 per cent. solution of potash in a flask fitted to a proper condenser, until all the ammonia is distilled over. It may be necessary to add water once or twice, and redistil; then 50 cc. of a strongly alkaline solution of permanganate of potash are added and distilled; the ammonia in the distillates is estimated by "Nesslerising." Mr. Wanklyn gives the following figures as yielded by a genuine tea—

	Mgrms.
Free Ammonia, ...	0·28
Albuminoid Ammonia, ...	0·43
	0·71

100 mgrms. of genuine tea, sent to the writer by Dr. Shortt, of Madras, yielded total ammonia ·81; but this is a method which has not been accepted by chemists, although it has some value.

§ 203. *Determination of Tannin.*—The methods proposed for the determination of tannin are very numerous. Four only, however, require any notice here—viz., the gelatine process, the copper process, Mr. Allen's acetate of lead process, and Löwenthal's process.

(1.) *By Gelatine.*—The best process by gelatine is decidedly that which dispenses with the drying and weighing of the precipitate. A solution of gelatine is carefully made by first soaking the gelatine in cold water for twelve hours, then raising the heat to 100°, by placing the bottle on the water-bath (the strength should be about three per cent.), and finally about ·8 per cent. of alum should be added. A portion of the solution thus prepared is put into an alkalimeter flask (*e.g.*, Schuster's), and carefully weighed. A solution containing a known quantity of tannin is now titrated with the gelatine until a precipitate no longer occurs; the flask is reweighed, and the loss shows approximately the strength of the solution. One or two more exact determinations will be required to get the correct value. It is necessary to allow the precipitate now and then to settle, and a few drops of the supernatant fluid should be placed on a watch-glass, to which a drop of gelatine may be added, and thus the point of saturation ascertained. The tannin in a decoction of tea is, of course, estimated on precisely similar principles.

(2.) *Copper Process.*—When a single determination of tannin is required it is best to precipitate by copper-acetate. 2 grms. of tea are boiled for an hour in 100 cc. of water, the solution filtered, the filtrate boiled, and while boiling 20 to 30 cc. of solution of copper acetate [1 : 20] added. The precipitate is collected, dried, burnt to an ash, oxidised with nitric acid, and again ignited and weighed. 1 grm. of $CuO = 1·3061$ of tannin, if Eeler's* figures be accepted; if Woolf's,† then 1 grm. $CuO = 1·304$ tannin.

(3.) *Mr. Allen's Lead Process.*—A filtered solution of lead acetate ·5 per cent., a solution of 5 mgrms. of pot. ferridcyanide, 5 cc. of strong ammonia water, and 5 cc. of pure water, and lastly, solution of pure tannin (·1 per cent.) are required. The process essentially depends upon the precipitation of tannin by lead acetate, and using ammoniacal pot. ferridcyanide as an indicator. The latter agent strikes a pink colour with tannin. The solution is standardised by taking a known volume of the lead solution,

* *Dingler's Poly. Journ.*, 229, 81.
† *Zeitschrift f. An. Chem.*, 1, 104.

and dropping in the tannin liquid until a small portion filtered gives a pink colour with the indicator.

Tea is tested in a precisely similar manner. Mr. Allen's method is tolerably speedy and accurate; the writer has, however, found the final reaction somewhat difficult to observe.

(4.) *Löwenthal's Process.*—Up to the present time this method (originally worked out for barks) is the best we possess; it depends on the oxidation by permanganate, and indigo is used as an indicator. It not alone gives us the tannin, but the amount of other astringent matters as well. The following solutions are required :—

(1.) A solution of potass. permanganate, 1·333 grms. per litre.
(2.) Precipitated indigo, 5 grms. per litre.
(3.) Dilute sulphuric acid (1 : 3).
(4.) A solution of gelatine, 25 grms. to litre, saturated with table-salt.*
(5.) A saturated solution of pure salt, containing 25 cc. of sulphuric, or 50 cc. of hydrochloric acid per litre.

The analysis as applied to the determination of tannin in barks is performed thus :—10 grms., say, of sumach are taken and exhausted by boiling with water, and the solution made up to 1 litre; of this infusion, 10 cc. are mixed with 75 cc. of water, 25 cc. of the indigo solution added, and 10 cc. of the dilute sulphuric acid. The permanganate solution is run drop by drop from the burette with constant stirring, till the blue colour changes to yellow, when the amount of permanganate used is noted (x). The same process is repeated with indigo and sulphuric acid, and the amount read off (y); subtracting y from x = total astringent matters. The permanganate oxidises both tannin and indigo; but the tannin being the easier to oxidise, is consumed first. In order to obtain accurate results, the proportion of indigo should be such as to require about twice the quantity of permanganate which would be consumed by the tannin alone. Thus, if indigo alone requires 10 cc. of permanganate to decolorise it, the indigo and tannin together must not take more than about 15 cc.; if it does so, the tannin must be diluted accordingly. The total astringent matters being known, the next step is to throw the tannin out, and estimate the gallic acid and impurities. 100 cc. of the infusion are mixed with 50 cc. of the salted gelatine infusion; after stirring, 100 cc. of the salt acid solution are added, and the mixture allowed to stand

* Löwenthal prepares the solution by steeping 25 grms. of the finest Cologne glue in cold water over night; it is then melted on the water-bath, saturated with NaCl, and made up to 1 litre with saturated NaCl solution, filtered, and kept well corked.

for twelve hours It is then filtered, and an aliquot part of the filtrate is oxidised by permanganate and indigo, as before.

Löwenthal gives the following example: 10 grms. of sumach were boiled in 750 cc., and after cooling made up to one litre:—

		Permanganate.
(1.) 10 cc. of sumach infusion, 25 cc. of indigo solution	consumed,	16·6
Do.,	repeated,	16·5
		33·1
50 cc. of indigo solution alone,		13·2
Total permanganate for 20 cc. of sumach,		19·9
(2.) 50 cc. filtrate from the gelatine, 25 cc. indigo solution,	consumed,	11·2
Do.,	repeated,	11·1
		22·3
50 cc. indigo alone,		13·2
Gallic acid and impurities,		9·1

Deducting 9·1 cc. from 19·9 cc. equals 10·8 cc. as permanganate, equivalent to the tannin of 20 cc. of sumach infusion, or 0·2 grm. of dry sumach. It is well to ascertain the value of the permanganate solution by oxalic acid, adopting the numbers given by Neubauer and Oser—viz., that 0·063 oxalic acid is equal to 0·04157 gallo-tannic and ·062355 quercitannic acids. Should it be preferred to use tannin, the purest commercial tannin must be precipitated by lead, the precipitate freed from lead in the usual way, and the solution of pure tannin then evaporated to complete dryness, and a solution of convenient strength made. The process requires but little modification to be applicable to tea.

The amount of tannin in genuine teas seems to be variable, S. Jauke, using the acetate of copper process, has determined the tannin in eighteen samples of black tea, and found as a maximum 9·142 per cent., as a minimum 6·922 per cent., and as a mean 8·1 per cent. Three samples of green tea gave 9·94, 8·56, and 9·57 per cent. Mr. Wigner, as a sample of very astringent teas, gives the following:—

	Per cent.
Moyone young Hyson,	39·0
Very choice Assam,	33·0
Indian young Hyson,	39·0
Assam tea from Dr. M'Namara's garden,	27·7
Caper, mixed,	42·3

Exhausted tea leaves yield from 2 to 4 per cent. of tannin. A tea giving only 6 per cent. of tannin is to be regarded as suspicious, but care must be taken not to rely upon any single indication.

§ 204. *The Extract.*—The extract is a measure of the soluble matter in tea. Peligot exhausted the leaves and then redried them, and thus estimated the soluble matter by difference. Wanklyn, however, has proposed a more rapid and convenient method. It consists in taking 10 grms. of tea, and boiling with 500 cc. of water, the flask being adapted to a Liebig's condenser. When 50 cc. are distilled over, the process is stopped, and the 50 cc. returned to the flask; 50·3 grms. of the hot strained liquid are then weighed out and evaporated to dryness. Wigner boils with a vertical condenser for an hour, and finds that 1 per cent. strength yields the most constant results. Perhaps, on the whole, the best process is the following:—Place one part of tea in 100 of water, boil for one hour with a vertical condenser, and then take an aliquot part of the filtered liquid for evaporation. In every case the time occupied in boiling, and the strength, should be mentioned in reporting, for two analysts operating by different methods may differ as much as 6 or 8 per cent.—the soluble matter not being entirely removed for a very long time. Since the substances that are at once dissolved are really those upon which its commercial value depends, it is a question whether it would not be better simply to pour boiling water on the leaves, let the infusion stand for one hour, and then estimate the extract, calling it *extract of infusion.*

Any addition of exhausted leaves lowers the percentage of extract. The following are some determinations of extract:—

	Per cent.	Analysed by
Java tea, dried, . .	35·2	Peligot.
,, not dried, . .	32·7	,,
Pekoe, ordinary, dry, .	41·5	,,
,, undried, . .	38·0	,,
Gunpowder, dry, . .	51·9	,,
,, undried, .	48·5	,,
,, dry, . .	46·9	,,
,, undried, .	50·2	,,
Moyone Gunpowder, .	40·7	Wigner.
,, .	39·3	,,
,, .	38·5	,,
,, .	37·9	,,
,, .	33·3	,,
Imperial, dry, . . .	43·1	Peligot.
,, not dried, . .	39·6	,,
,, dry, . . .	47·9	,,
not dried, . .	44·0	,,

	Per cent.	Analysed by.
Hyson, dry,	47·7	Peligot.
" not dried,	43·8	"
Hyson skin, dry,	43·5	"
" not dried,	39·8	"
Congou,	36·8	"
" dried,	40·9	"
" bon,	40·7	"
" " dried,	45·0	"
"	33·0	Wigner.
"	29·8	"
"	29·8	"
"	26·2	"
"	26·1	"
Caper, dried,	39·3	Peligot.
" not dried,	35·8	"
"	37·9	Wigner.
"	37·7	"
"	32·4	"
"	30·0	"
Assam, dried,	45·4	Peligot.
" not dried,	41·7	"
"	33·3	Wigner.
Hyson,	36·8	"
Moyone Yôung Hyson,	44·8	"
Tea direct from China, dry,	41·7	Wanklyn.
" "	40·2	"
" "	41·2	"
Indian Tea, dry,	33·9	A. Wynter Blyth
"	43·8	Wigner.
Broken Indian,	43·4	"
Indian Souchong,	32·5	"
Scented Orange Pekoe,	34·2	"
Manuna, fine,	37·0	"
Himalayan Tea,	38·6	Wanklyn.
"	35·4	"

Since the extract of genuine tea appears to vary from 26 per cent. up to more than 40 per cent., it is unfortunately of no very great value for purposes of estimation. The extract, after being weighed, is burnt up to an ash, which will always be found to be heavy, rich in alkaline salts, and varying usually from 4 to 7 per cent.

§ 205. *The Ash.*—The percentage of total ash is taken by burning up 1 to 5 grms. of the tea in a platinum dish. The leaves readily ignite, and the operation may take place at a very low temperature, so that there is, with care, very little volatilisation of chlorides. The comparative composition of the ash of fresh and of exhausted tea leaves is shown in the following table :—

TABLE XXIII.

	Zoller.	Hodges.		Zoller.	Wigner.	
	Ash of fine young Himalaya Tea.	Tea from Cachar (indigenous).	Tea from Cachar (hybrid).	Exhausted Tea Leaves.	Ash of a number of Mixed Black Teas	Ash of a number of Mixed Green Teas
Potash, . .	39·22	35·200	37·010	7·34	30·92	28·42
Soda, . .	0·65	4·328	14·435	0·59	1·88	2·08
Magnesia, . .	6·47	4·396	5·910	11·45	...	...
Lime, . .	4·24	8·986	5·530	10·76	...	...
Oxide of Iron, .	4·38	2·493	2·463	9·63	...	...
Manganous Oxide,	1·03	1·024	0·800	1·97	...	...
Phosphoric Acid,	14·55	18·030	9·180	25·41	...	...
Sulphuric Acid, .	trace.	5·040	6·322	trace.	4·88	5·66
Chlorine, . .	0·81	3·513	2·620	trace.	...	...
Silica and Sand,	4·35	0·500	1·300	7·57	1·70	7·50
Charcoal, . .	...	2·900	1·830	...	..	...
Carbonic Acid, .	24·30	13·590	12·600	25·28	11·60	6·43
	100·00	100·00	100·00	100·00		
Percentage of total Ash soluble in water,	...	...	...	...	57·00	52·85

The ash, on being cooled and weighed, is next boiled up with a little water, the soluble portion filtered from the insoluble, and washed in the ordinary way. The filtrate is evaporated to dryness, very gently ignited, and returned in percentage as soluble ash. The insoluble portion is next treated with acid, and the remaining sand dried, ignited, and weighed. The alkalinity of the soluble portion should also be taken, and may be returned as potash. This simple examination of the ash, consuming very little time, gives tolerably well all the information afforded by a complete and exhaustive analysis. The table (XXIV.) shows a few percentages of ash, and may be compared with the percentages of beech, bramble, &c.

All the analyses hitherto published show that the percentage of ash in genuine tea never reaches 8 per cent. An ash beyond 8 per cent., calculated on the dried tea, is certainly adulterated. In the same manner, all genuine tea possesses a soluble ash not

TABLE XXIV.

	Total Ash. Per cent.	Ash soluble in Water. Per cent.	Ash soluble in Acid. Per cent.	Silica.	Potash.	Authority.
Average of 17 ordinary Teas from original chest, consisting of 2 Indian, 12 Congous, 2 Gunpowders, and 1 Hyson, . .	5·75	3·07	2·25	0·43	1·38	G. W. Wigner.
Maximum, . .	6·03	3·35	2·87	0·76	1·88	,,
Minimum, . .	5·53	2·75	1·99	0·15	1·17	,,
Average of 25 special Teas, . .	5·95	3·33	2·09	0·53	1·38	,,
Maximum, . .	7·02	3·88	2·68	1·67	1·96	,,
Minimum, . .	5·17	2·64	1·33	0·04	1·08	,,
Genuine Indian Tea, .	5·61	2·90	...	...	...	A. Wynter Blyth.
Common Tea, . .	5·92	3·55	...	...	...	Wanklyn.
Paraguay Tea, . .	6·28	4·22	...	...	...	,,
Average of 7 Teas, .	5·75	...	...	...	...	A. S. Wilson.
,, 9 ,, .	5·66	3·00	...	...	...	A. H. Allen.
Horneman's p. black,	5·30	3·50	...	...	...	,,
,, green,	5·60	3·80	...	...	...	,,
Ambrosial black, .	5·60	3·40	...	...	...	,,
Genuine blk., 2s. 6d. lb.,	5·60	3·09	...	...	...	,,
,, ,,	5·70	3·28	...	...	...	,,
,, ,,	6·02	3·26	...	...	...	,,
,, ,,	6·34	3·20	...	...	...	,,
,, ,,	6·10	3·96	...	...	...	,,
,, ,,	5·75	3·06	...	...	...	,,
,, 3s. lb., .	5·50	3·55	...	...	...	,,
Broken leaf, with stalks,	5·40	2·80	...	...	...	,,
Caper (4·8 silica), .	11·40	1·50	...	...	...	,,
Mixed dry exhausted leaves from various Teas, . .	4·30	0·52	...	..	...	,,
Coffee leaves, . .	10·32	3·77	...	...	...	,,
Beech, . . .	4·52	2·00	...	...	...	Wanklyn.
Bramble, . . .	4·53	1·84	...	...	...	,,
Raspberry, . .	7·84	1·72	...	...	...	,,
Hawthorn, . .	8·05	3·78	...	...	...	,,
Willow, . . .	9·34	4·16	...	...	...	,,
Plum, . . .	9·90	5·66	...	...	...	,,
Elder, . . .	10·67	3·19	...	...	...	,,
Gooseberry, . .	13·50	7·83	...	...	...	,,

less than 3 per cent. For examples of obviously impure ashes, Mr. Wigner's paper may be quoted from again :—

	Total Ash.	Soluble in Water.	Soluble in Acid.	Silica.	Alkali calculated as Potash.	Extract.
Gunpowder,	19·73	1·00	6·15	12·58	0·14	37·78
Caper, .	14·44	1·95	2·47	10·02	1·03	35·45
	15·20	1·69	5·35	8·16	0·61	31·60
	15·08	1·96	5·65	7·47	0·73	35·60
	12·74	2·68	5·44	6·62	1·04	...
	14·60	2·67	5·67	6·06	1·04	...

All these teas, although imported in this state, are evidently mixed with sand to a considerable extent.

§ 206. *Determination of Gum.*—If it is necessary to determine the gum in tea, as sometimes happens, the aqueous decoction should be evaporated nearly to an extract, and the residue treated with methylated spirit, filtered, and washed with the spirit. The gum is dissolved off the filter by the aid of hot water, and the solution evaporated to dryness, and weighed; it is then ignited to an ash, and the mineral deducted from the total weight.*

§ 207. *General Review of the Adulterations of Tea.*—The most frequent are, certainly, the addition of sand, generally strongly impregnated with iron, the addition of foreign and exhausted leaves, and the addition of astringent principles, such as catechu, &c. All these adulterations must take place abroad, there being no evidence that a single hundredweight of tea has been tampered with in England,—the blame *may* lie with the home-traders, but proof is wanting. On the other hand, it not unfrequently happens that cargoes of tea recovered from sunk vessels, or teas damaged in some other way, are sold and blended by wholesale manufacturers with those that are genuine. Such samples contain usually

* H. Hager is (*Pharm. Central. Halle*, 1879, 258) the author of a general process of analysis, which possesses some good points: 10 grms. of tea are infused in 100 cc. of warm water, and allowed to stand for two days; the solution is poured off, and another 100 cc. of water added to the partially-exhausted leaves, which are then unrolled and botanically examined. 50 cc. of the solution are evaporated to dryness; 10 cc. of the solution should give no turbidity in the cold when an equal volume of alcohol is added. For the estimation of theine, 10 grms. of tea, 3 grms. of sodic carbonate, and 3 grms. of litharge are made into a paste with 10 grms. of water dried up and extracted with chloroform. For the special detection of catechu, ·1 grm. of tea is extracted by 100 cc. of boiling water. This solution is boiled with excess of lead oxide, and the filtrate (which must be clear) mixed with a solution of silver nitrate. Pure tea gives only a slight grey-black troubling of metallic silver, but tea adulterated with catechu a strong yellow flocculent precipitate.

an excess of salt, and show more or less evidence of the addition of exhausted leaves.

The facing of tea is rapidly decreasing. There has been much dispute as to whether this is to be considered an adulteration or not; a thin film of graphite, or any other harmless substance, in such quantity as to add no appreciable weight, can hardly be called adulteration. Each case, however, must be judged of by its merits. A small addition of such a substance as catechu, to impart astringency, is probably frequent, and difficult of detection. Any amount present, to the extent of 3 per cent. or over, is shown by precipitating an infusion of the tea with a slight excess of neutral lead acetate, filtering, and adding a little dilute ferric chloride solution. If catechu be present there is a bright-green colour, and ultimately a precipitate of a greyish-green colour. [See also Hager's method, footnote, p. 339.] The same infusion filtered from the lead precipitate gives a copious precipitate with argentic nitrate. Mr. Allen has pointed out the advantage of his lead process in cases of adulteration with catechu, and it is self-evident; for catechuic acids possess a precipitating power so widely different from that of tannin, that, if reckoned as tannin, there are always anomalous results, indicating a much higher astringency than could possibly exist,—*e.g.*, a sample of brown catechu examined in this way, and reckoned as tannin, gives the paradoxical number of 11 per cent.

Soluble iron salts, alkaline carbonates, and other substances, are stated to be occasionally added, but no conviction relative to these appears to be on record. The soluble iron salts may, of course, be dissolved from the tea leaves by a little cold dilute acetic acid, and the liquid tested in the usual way; there is then no confusion between the iron naturally present and that added.

§ 208. *Bohemian Tea.**—It would seem that for some time there has been cultivated in Bohemia the *Lithospermum officinale*, the common "Gromwell" of our country, and the leaves have been dried and sold as *Thea Chinensis*, under the name of "Bohemian Tea." They have also been used for the purpose of adulterating Chinese tea. The "Gromwell" is a plant belonging to the borage order, growing in dry and stony places, from a foot to a foot and a half high. The flower is greenish-yellow, the stem erect and branching, and the leaves are lanceolate, hairy beneath, with bulbous adpressed bristles above. They are totally unlike tea leaves, and the hairiness itself would be diagnostic of a leaf other than that of tea. The chemical composition is also entirely different. The mineral constituents are excessive, and there is neither any alkaloid nor any essential oil.

The average composition of "Bohemian Tea" is as follows:—

* A. Belohouben: *Chem. Centralbl.*, 1880, p. 152.

Cellulose,	5·9637
Tannin,	8·2547
Fat,	9·2910
Other nitrogen-free organic substances,	26·4941
Albuminous matters,	24·5406
Ash,	20·5960
Water,	4·8599

BIBLIOGRAPHY RELATIVE TO TEA AND THEINE.

ALLEN, A. H.—*Pharm. Journ.*, 1873; *Chem. News*, vol. xxx., 1874.
BALL.—"Account of the Cultivation and Manufacture of Tea in China."
BERTHEMOT u. DECHASTELUS.—*Journ. Pharm.* (2), xxvj. 63.
BLYTH, A. WYNTER.—Micro-Chemistry, as applied to the Detection of Foreign Leaves in Tea, *Analyst*, June, 1877; Indian Tea, *Journ. Chem. Soc.*, 1875, 385.
BOLLEY—*Journ. Pract. Chem.*, xciv. 65.
BROWN, DR. CAMPBELL.—*Journal Chem. Soc.*, 1875, 1217.
CAZENEUVE, PAUL, and O. CAILLOT.—*Bull. Soc. Chem.* [2], xxvij. 199.
COMMAILLE.—*Journ. de Pharm. d'Anvers*, 1876, 121.
DAVIS.—*Journ. Pharm. et Chim.*, 3e série, 1853, t. xxiv., p. 228.
FORTUNE, ROBERT.—*Repert. de Pharm.*, 1856, t. vij., p. 117.
GAROT.—*Journ. Pharm.* (2). xii. 234.
GUIBOURT.—*Journ. Chim. Méd.*, 2e série, 1844, t. x., p. 459.
GUNTHER.—*Journ. Prac. Chem.*, x. 273.
HERZOG.—*Ann. Chim. Pharm.*, xxvj. 244; xxix. 271.
HAGER, H.—*Pharm. Centralhalle*, 1879, 258.
HASSALL.—"Food: the Detection of Adulterations in." Lond., 1871.
HLASIWETZ u. PFAUNDLER.—*Ann. Chem. Pharm.*, lxxxii. 197; cxii. 96; *Journ. Pract. Chem.*, xciv. 65.
HODGES.—*Chem. News*, xxx. 125.
HUSEMANN.—Die Pflanzenstoffe, Berlin, 1871.
JANKE, L.—Beilage zu dem Veröffentlich. des Kaiser-deutschen-Gesundheitsamtes, p. 169.
JOBST, C.—*Ann. Chem.*, xxv. 63.
LEGRIP and PETIT.—*Bull. Soc. Chim.*, 500.
LETHEBY.—*Med. Press and Circular*, 1871, p. 415.
MARTIUS.—*Kastn. Arch.*, vii. 266; *Ann. Chim. Pharm.*, xxxvj. 93.
MARKOWNSKOFF, B. W.—*Deut. Chem. Ges. Ber.*, ix. 1312.
MARCHAND, E.—*Journ. Chim. Méd.*, 2e série, 1844, 24.
MEDHURST.—*Parl. Papers*, 1871.
NICHOLSON.—*Chem. Soc. Journ.*, ix. 321.
OUDRY, GEIGERS.—*Mag. Pharm.*, xix. 45.
PELLETIER.—*Journ. Pharm.*, 2, xii. 229.
PELIGOT.—*Ann. Chim. Phys.* (3), xi. 138.
PFAFF u. LIEBIG.—*Schweigg. Journ. Chem. Phys.*, lxi. 487; lxiv. 372; *Ann. Chem. Pharm.*, i. 19.
ROCHLEDER.—*Ann. Chem. Pharm.*, l. 231; lxiii. 201; lxix. 120; lxxi.; *Journ. Pract. Chem.*, li. 401.
STENHOUSE.—*Phil. Mag. J.*, xxiii. 426; xlii. 21; *Chem. Soc. J.*, ix. 33.
STRECKER.—*Ann. Chem. Pharm.*, cxviii. 151.
WANKLYN, J. A.—"Tea, Coffee, and Cocoa." London, 1874. *Chem. News*, xxviij. 186.
WARRINGTON.—*Chem. Soc. Journ.*, 1858.
WIGNER.—*Analyst*, 1876; also *Pharm. Journ.*, 3rd series, 1874.

MATÉ.

§ 209. "The *Maté*, or Paraguay Tea Tree (*Ilex maté paraguayensis*), is a small tree, belonging not to the family of the *Ilicicæ*, as stated by some, but to the *Celastrineæ*; it reaches in height ordinarily 4 or 5 metres, sometimes 7. Its trunk is about 20 cm. in circumference, and is covered by a whitish bark. The leaves are oblong, cuneiform, obtuse, and finely dentate. It has ancillary, multipartite peduncles, calyx tetrasepalous, the corolla with four petals in the form of a crown, style none, stigma 4 fid, fruit a four-celled berry. The plant grows very abundantly in Paraguay, North Corrientes, Chaco, and South Brazil, where it forms woods called 'Yerboles.'"

Maté is prepared in Paraguay thus:—The entire trees are cut down, and the small branches and shoots are taken with the leaves, and placed in the *tatacûa*, a plot of earth about 6 feet square, surrounded by a fire, where the plant undergoes its first roasting. From thence it is taken to the *barbacua*, or grating supported by a strong arch, underneath which burns a large fire. Here it is submitted to a particular torrefaction, determined by experience, which develops the aromatic principle. Then it is reduced to a coarse powder in mortars formed of pits dug in the earth, and well rammed. It is next put into fresh bullock skins, well pressed, and placed in the sun to dry. The packages (*tercois*) thus obtained weigh from 90 to 100 kilograms, and have an average commercial value of 1 to 2 dollars the kilogram.

Senõr Araté gives an analysis of maté—

	In 100 parts.
Organic combustible substances,	91·685
Ash,	8·315
The ash contains—	
Lime (CaO),	12·344
Magnesia,	11·395
Soda,	7·281
Potash,	2·984
Manganese dioxide,	2·500
Ferric oxide,	3·410
Sulphuric acid,	0·926
Hydrochloric acid,	0·716
Phosphoric acid,	5·540
Carbonic acid,	8·150
Sand, silica, carbon, and loss,	44·754

The enormous relative quantity of sand is a result of the mode of preparation in excavations made in the soil. The plant contains—

Principles soluble in ether,		9·820
,, ,,	alcohol,	8·432
,, ,,	water,	26·208
,, ,,	water acidulated with HCl,	7·260
,, ,,	in solution of caustic soda,	16·880
Cellulose,		13·280
Water,		9·000
Sand,		9·120
		100·00

Theine averages 1·3 per cent. The tannin of maté is peculiar; it does not tan hides, and requires a special method for its estimation; it amounts to about 16 per cent. Maté also contains a large quantity of a peculiar fatty matter. Maté does not exalt the peripheric nerves like tea, nor the cerebric like coffee, but appears to have, in some degree, a narcotic action. The usual way of taking it is by sucking it up through a reed called a "bonibilla."

MM. d'Arsenval and Couty have recently inquired into the action of maté, administering it to dogs by injection into the stomach. They found it diminish the carbon dioxide and oxygen of the arterial and venous blood to a considerable extent, sometimes to a third or even half the normal quantity. This action, which is less intense during digestion, and has no necessary relation to phenomena of excitation of the sympathetic nerve-system, is somewhat obscure as to its "mechanism;" but its existence proves directly the importance and nutritive value of the aliment in question.

A species of *Ilex*—viz., *Ilex cassiva*, employed as a tea in Virginia, has been analysed by M. Ryland and T. Brown, who found

Volatile oil,	0·011
Wax and fatty matter,	0·466
Resin,	3·404
Chlorophyll,	2·491
Theine,	0·122
Tannin,	2·409
Colouring-matter soluble in alcohol,	4·844
Extractive matter soluble in alcohol,	10·149
Extractive matter insoluble in alcohol,	4·844
Amidon and pectine,	15·277
Fibre,	33·827
Ash,	3·995

COFFEE.

§ 210. The coffee berry is the seed dried, and deprived of its fleshy coverings, of the *Caffea arabica*, Nat. Ord. *Cinchonaceæ.*

Before use the berries are roasted to a chocolate brown, and then ground in a mill.

Microscopical Structure.—The main portion of the berry is composed of strong, angular, thick-walled cells, as represented in fig. 39, *a*. The figure is an accurate representation of what was seen in a fine section of a sample of unroasted coffee, but this particular sample shows the cell divisions much more distinctly than usual. When the coffee has been roasted, the usual appearance of these cells is that of very dark, small, irregularly-triangular masses, representing the contracted cell-contents set in a transparent matrix, in which it is difficult to trace the cell-walls. The cellular elements of the seed, more especially in the outer layers, are impregnated with drops of oil. A thin, tough, Japanese-paper-like membrane (fig. 39, *b*) may be detached from the berry, and is found to be composed of a series of spindle-shaped fibres attached to a tissue which shows signs of fibrillation, and is probably composed of a number of very fine fibres, adhering by their edges, so as to form a continuous sheet.

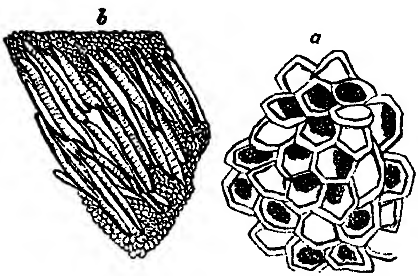

Fig. 39. Coffee tissues, × 170.

The microscopical structure just described separates and distinguishes coffee at once from all other known berries or seeds, while the tissues of roots, such as chicory (consisting of loose, thin-walled, vegetable cells, with a greater or less admixture of large spiral vessels), are entirely different, and may be said, indeed, to be built on a different plan.

§ 211. *Chemical Changes during Roasting.*—The effect of roasting is to drive off a large quantity of water, to volatilise a small quantity of theine, to change a portion of the sugar into caramel, to rupture the cell-layers containing fat and albumen, and to swell the berry by the extrication of gases, consisting mainly of carbon dioxide. There is also developed a fragrant aromatic substance, a single drop of which is sufficient to scent a large room with the peculiar coffee odour; the best temperature for the production of this aroma is 210°. That during roasting there is an actual loss of theine, is easily proved by holding a glass plate over the heated berries; in a very little time crystals of the alkaloid condense. Tenneck found in unroasted coffee ·75 per cent., and in the same roasted, ·42 per cent. theine. It would

appear that roasted coffee gives up more to water than does raw coffee; for Cadet found that beans roasted to a light brown yielded to water 12·3 per cent.; to a nut-brown, 15·5 per cent.; and to a dark-brown, 21·7 per cent. Vogel also gives the soluble matters in raw coffee as 28 per cent.; and in roasted, 39 per cent. The amount of sugar changed is always considerable; thus, Graham and Stenhouse found the following differences in the percentage of sugar between the raw and roasted coffees:—

	Raw. Per cent.	Roasted. Per cent.
Highest amount, ...	7·78	1·14
Lowest amount, ...	5·70	...
Average of twelve specimens grown in different places, . . .	0·97	0·26

König has studied the changes taking place in roasting, and his views and experiments are as follows* :—

300 grms. of coffee-berries containing 11·29 per cent. water gave, on roasting to a light brown colour, 246·7 grms. of roasted coffee, containing 3·19 per cent. water. We have therefore—

1. Taken 300 grms. coffee berries, .	=266·15 grms. dry substance.
2. Obtained 246 grms. roasted coffee,	=238·83 ,, ,,
Then loss, 53·3 grms., . . .	=27·32 grms. dry substance.
Or in per cent., 17·77, . . .	= 9·11 per cent. organic substance.

Hence, in roasting, 8·66 per cent. of water, and 9·11 per cent. of organic substances have been lost. This is divided among the constituents of coffee as follows. (See Table XXV.)

§ 212. *Constituents of Coffee.*—The main properties of coffee are apparently due to four distinctive substances:—(1.) Unessential oil, not yet completely studied; (2.) caffeo tannic acid; (3.) theine or caffeine; (4.) a concrete oil or fatty substance.

Theine, or *Caffeine*, is described at p. 316.

Caffeo-tannic Acid, $C_{14}H_8O_7$, was first observed by Pfaff, in the seeds and leaves of the coffee plant; it also occurs in the root of the *Chiococcu racemosa*, and in the leaves of the *Ilex paraguayensis*, S. Hil. It may be separated from coffee by fractional precipitation of the infusion with acetate of lead. The precipitate, at first falling, consists of citrate with caffeo-tannate of lead; but later on, the latter occurs alone, and can be washed with water and decomposed by SH_2 in the usual way. Caffeo-tannic acid thus obtained is a brittle, yellowish mass, easily powdered, and of feeble acid reaction. It is supposed to exist in the plant in combination with potash and theine. It is scarcely soluble in ether, but dissolves easily in water or in alcohol. The solution gives a

* Nahrungs-und Genussmittel, Bd. ii., 479.

TABLE XXV.

	Total matters soluble in Water.	Nitrogen. Nitrogen-ous Substances.*	Theine.	Fat.	Sugar.	Other N.-free Substances.	Cellulose.	Ash.	Water.
1. In 300 grms. unroasted coffee,	82·32	5·610 = 28·69	3·540	39·69	9·75	90·88	83·16	10·44	33·87
2. In 246·7 grms. roasted coffee,	73·29	5·698 = 29·43	3·403	38·56	3·23	94·49	59·87	9·85	7·87
Then in the last more + or less −	−9·03	+(0·078)? + (0·74)	−·137	−1·13	−6·52	+3·61	−23·29	−0·59	−26·00
Or in per cents. of the original quantity,	−10·9%	+ +? +?	−3·1%	−2·1%	−66·9%	+3·9%	−28·0%	−5·7%	−76·7%
The percentage composition of the dry substance was as follows:—									
1. Unroasted coffee,	30·93	2·21 = 11·43	1·33	14·91	3·66	34·55	31·24	3·92	...
2. Roasted,	28·36	2·38 = 12·31	1·42	16·14	1·35	39·84	25·07	3·87	...
Or reckoned on the natural substance,									
1. Unroasted coffee,	27·44	1·87 = 8·43	1·18	13·23	3·25	31·52	27·72	3·48	11·19
2. Roasted,	27·45	2·31 = 12·05	1·38	15·63	1·32	38·41	24·27	3·75	3·19

* Theine subtracted.

dark-green colour with chloride of iron, or if dissolved in aqueous solution of ammonia, the alkaline earths, or the alkalies, a reddish-yellow or yellow colour. If caffeo-tannic acid be decomposed with 3 parts of solid potash, the end product is protocatechuic acid. If it be boiled with 5 parts of potash-lye (1·25 specific gravity) for three-quarters of an hour, and then neutralised by sulphuric acid, caffeic acid ($C_9H_8O_4$) crystallises out, and can be obtained in straw-yellow prisms and plates by recrystallisation from hot water. It colours chloride of iron grass-green, is oxidised by nitric acid into oxalic acid, and is decomposed by potash into protocatechuic and acetic acids.

Coffee Fat.—The coffee fat can be obtained from an alcoholic extract of coffee; part separates on cooling the fluid to 0°, the rest on dilution with water. It is white, without odour, of a buttery consistence, melting at 37°·5, and becomes rancid on exposure to the air. According to Rochleder (*Wien Akad. Ber.*, xxiv. 40), it contains the glyceride of palmitic acid and of an acid of the composition $C_{12}H_{24}O_2$.

C. O. Cech * exhausted 50 lbs. with alcohol and ether, and obtained 1,200 grms. of a thick green fluid oil, and after a time fine crystals of theine separated. After six months the oil, although in closed flasks, began to be turbid, and gradually little groups of crystals separated and sank to the bottom. After the lapse of three years, the flask was found to be about two-thirds filled with crystals of the more solid fats, but the upper layer was beautifully green.

There are also citrates, and probably other organic acids and nitrates in coffee. J. Buig found in raw dry coffee ·054 per cent. of nitrate of potash, in roast ·041 per cent.

The following table gives the general composition of various commercial varieties of coffee :—

	Gummy Matter.	Caffeine.	Fat.	Tannic and Caffeo-tannic Acids.	Cellulose.	Ash.	Potash.	Phosphoric Acid.
Finest Jamaica Plantation,	25·3	1·43	14·76	22·7	33·8	3·8	1·87	0·31
Finest Green Mocha,	22·6	0·64	21·79	23·1	29·9	4·1	2·13	0·42
Ceylon Plantation,	23·8	1·53	14·87	20·9	36·0	4·0	...	0·27
Washed Rio,	27·4	1·14	15·95	20·9	32·5	4·5	...	0·51
Costa Rica,	20·6	1·18	21·12	21·1	33·0	4·9	...	0·46
Malabar,	25·8	0·88	18·80	20·7	31·9	4·3	...	0·60
East Indian,	24·4	1·01	17·00	19·5	36·4	...	...	...

* *Journ. für Prak. Chemie*, xxii. 398.

Some analyses of Dragendorff may be also quoted :—*

TABLE XXVI.

	Caffeine. Per cent.	Ash. Per cent.	Potash. Per cent.	Phosphoric Acid. Per cent.
1. Brown Preanger, ...	0·71	4·80	...	0·42
2. Mocha, yellow, very fine, .	0·64	4·06	2·13	0·42
3. Menado, yellow, . . .	1·22	4·03	...	0·39
4. ,, blue, . . .	1·38	4·11	...	0·36
5. Alexandrian Mocha, . .	0·84	4·19	...	0·44
6. Jamaica Plantation, very fine,	1·43	3·83	1·87	0·31
7. Surinam, 1st quality (Java), .	1·78	4·39	...	0·56
8. Preanger, ...	0·93	4·36	...	0·35
9. Surinam, 2nd quality (Java), .	1·04	4·77	...	0·33
10. Ceylon Plantation, . . .	0·78	4·02	...	0·31
11. Yellow Java, ...	0·88	4·31	...	0·28
12. West Indian (Java), . .	1·22	4·21	...	0·32
13. Mysore, ...	1·23	4·20	2·12	0·31
14. Malabar, ...	0·88	4·27	...	0·60
15. Java, ...	2·21	4·01	...	0·41
16. Costa Rica, ...	1·18	4·94	...	0·46
17. Ceylon Plantation, . . .	1·53	4·00	...	0·27
18. Washed Rio, ...	1·14	4·53	...	0·61
19. Native Ceylon, ...	1·14	4·65	...	0·72
20. ,, ,, 1st quality, .	0·87	4·65	...	0·41
21. ,, ,, 2nd ,,	1·54	4·80	...	0·44
22. African Mocha, ...	0·70	4·70	2·80	0·38
23. Jamaica, ...	0·67	4·82	2·83	0·42
24. Native Ceylon, 3rd quality, .	1·59	4·87	2·60	0·40
25. Santos, ...	1·46	4·81	2·67	0·48

§ 213. *Analysis of Coffee.*—The hygroscopic moisture, theine,

* There is also a very elaborate analysis of coffee made by Payen, at a date when food analysis was not so well understood as now. It is probably a fair approximation as regards the more important constituents, but the percentage of ash can hardly be correct.

Cellulose, ...	34·000
Water (Hygros.), ...	12·000
Fat, ...	10 to 13·000
Glucose, Dextrine, &c., ...	15·000
Legumin, ...	10·000
Caffeate of Potash and Caffeine, ...	3·5 to 5·000
Nitrogenous substance, ...	3·000
Free Caffeine, ...	0·800
Concrete Essential Oil, ...	0·001
Aromatic Fluid Essential Oil, ...	0·002
Ash, ...	6·697

gum, astringent principles, and ash are all determined precisely as in the case of tea.

The coffee fat may be conveniently estimated by putting a known quantity in the fat-extraction apparatus figured at page 67; the best solvent to use will be petroleum ether, since it has less solvent action on the theine than ether. When the process is finished, the petroleum is evaporated to dryness in a tared dish. As thus obtained, the fat is almost, but not quite, pure.

ADULTERATIONS OF COFFEE AND THEIR DETECTION.

§ 214. The sophistications usually enumerated are chicory, roasted wheat and beans, rye and potato flours, mangel-wurzel, acorns, lupine seeds, ground date-stones, and burnt sugar. The coffee is usually adulterated when in powder, but patents have been taken out for compressing ground coffee with chicory into the shape of berries.

The sophistication of coffee was at one time a regularly-organised industry; and there existed, some years ago, two manufactories in France—one at Lyons and the other at Havre—expressly established for the purpose of mixing coffee with burnt cereals and the scorched outer covering of cocoa. Without venturing to assert that coffee is at the present time adulterated in England with chicory alone, it is certain that other admixtures are of the greatest rarity.

A preliminary examination will in a few minutes detect, so far as chicory is concerned, whether it has been added or not. If the ground coffee be sprinkled on water, nearly the whole of it floats; if chicory be present, the chicory separates and sinks to the bottom, imparting a brown colour to the liquid. In this way, indeed, a tolerably complete separation of coffee and chicory may with care be obtained. The portions which sink to the bottom are, of course, examined microscopically. They are always soft to the touch, very different from the hard, gritty feeling of coffee particles; and put under the microscope, the difference of structure is at once apparent, for the loose, large cells of the chicory root, with dotted vessels and branching laticiferous ducts, are readily seen and appreciated.*

* Chicory is so readily detected that we scarcely require a direct chemical test. A. Franz has, however, pointed out that an infusion of coffee, when treated with copper acetate and filtered, yields a greenish-yellow filtrate; an infusion of coffee containing chicory yields, when similarly treated, a dark red-brown filtrate.—*Arch. Pharm.* [5], 298–302.

A method of detecting chicory has been described by C. Husson.

When chicory is mixed with coffee, the chemical composition of the mixture shows, in some particulars, a marked deviation from that of pure coffee.

Letheby's analysis of chicory is as follows :—

	Raw root.	Kiln dried.
Hygroscopic Moisture,	77·0	15·0
Gummy Matter,	7·5	20·8
Glucose or Grape Sugar,	1·1	10·5
Bitter Extractive,	4·0	19·3
Fatty Matters,	0·6	1·9
Cellulose, Inuline, and Woody Matter,	9·0	29·5
Ash,	0·8	3·0

Composition of the roasted root :—	(1.)	(2.)
Hygroscopic Moisture,	14·5	12·8
Gummy Matter,	9·5	14·9
Glucose,	12·2	10·4
Matter like Burnt Sugar,	29·1	24·4
Fatty Matter,	2·0	2·2
Brown or Burnt Woody Matter,	28·4	28·5
Ash,	4·3	6·8

The ash of these had the following composition :—

Chloride of Potassium,	0·22	0·45
Sulphate of ,,	0·97	0·98
Phosphate of ,,	1.41	1·37
,, Magnesia,	0·90	0·53
,, Lime,	0·40	0·81
Carbonate of ,,	0·10	0·26
Alumina and Oxide of Iron,	0·20	0·20
Sand,	0·70	2·20

Chicory influences the composition of coffee as follows :—

(1.) It decreases the gum, the latter seldom rising in chicory to more than 15 per cent., whilst in coffee it has not been found less than from 21 up to 28 per cent.

According to the latter, the chicory is often prepared by roasting with rancid fat. He discovers this by putting in a flask 10 grms. of chicory with 50 grms. of glycerine and 20 drops of hydrochloric acid, and the mixture is boiled and filtered. The filtrate is added to an equal volume of ether, and placed in a flask which, again, is put in a bath with boiling water. When pure ether-vapour rushes out of the bottle, the vapour is lit, and under the combined heat, the fatty matter rises to the surface of the glycerine, and is dissolved in the ether. When the flame diminishes in intensity, it is extinguished, and the ether allowed to evaporate spontaneously. On exposure to cold, fatty drops form gradually; these are examined by the microscope, and are drops of crystalline fats, such as are not yielded by pure coffee.

(2.) It increases in sugar, roasted coffee having seldom so much as 2 per cent. of sugar; whilst chicory, when roasted, usually has at least 8 or 9 per cent.

(3.) It decreases the fatty matter, the fat of chicory ranging from 1 to over 2 per cent., that of coffee from about 14 per cent. up to over 20 per cent.

(4.) It decreases the tannin and caffeo-tannic acids, chicory being destitute of tannin.

(5.) It decreases the caffeine, chicory possessing no alkaloid.

(6.) It profoundly modifies the constitution of the ash, especially by introducing silica, which is not a component of coffee ash. The main differences are thus as follows:—

	Coffee Ash. Per cent.	Chicory Ash. Per cent.
Silica and Sand,	.	10·69 to 35·88
Carbonic Acid,	14·92	1·78 to 3·19
Sesquioxide of Iron,	0·44 to 0·98	3·13 to 5·32
Chlorine,	0·26 to 1·11	3·28 to 4·93
Phosphoric Acid,	10·00 to 11·00	5·00 to 6·00
Total Soluble Ash,	75·00 to 85·00	21·00 to 35·00

Some approximate idea (although no accurate results) may be obtained of the amount of chicory present, if a careful determination of the soluble ash is made. If we take the soluble ash of chicory as 1·74, and that of coffee as 3 per cent., then the following table may be used:

TABLE XXVII.,—Giving the Theoretical Quantity of Soluble Ash, Corresponding to Various Admixtures of Chicory and Coffee.

Percentage of Chicory.	Percentage of Soluble Ash.	Percentage of Chicory.	Percentage of Soluble Ash.
5	2·94	50	2·58
10	2·88	55	2·56
15	2·82	60	2·52
20	2·79	65	2·50
25	2·74	70	2·48
30	2·70	75	2·46
35	2·67	80	2·43
40	2·64	85	2·41
45	2·60	90	2·40

By making standard infusions of pure coffee and chicory, and then taking the same weight of the suspected coffee, and com-

paring the colour, it is possible to obtain some idea of the quantity of chicory added

Leebody recommends this to be done as follows:—Take 1 grm. of the unknown mixture, and 1 grm. of a standard mixture of equal parts of chicory and coffee; remove all the colouring-matter from each sample, and make the extract of each up to the same bulk. Put 50 cc. of the filtered extract from the *unknown mixture* in the Nessler cylinder, and determine by trial how many cc. of the extract from the *standard* mixture, together with sufficient distilled water to make up the 50 cc., will give the same colour. In calculating the percentage of chicory present, closely accurate results are obtained in practice by assuming the tinctorial power of chicory to be three times that of coffee.—(J. R. LEEBODY, *Chemical News*, xxx. 243.)

Messrs. Graham, Stenhouse, and Campbell proposed to take the density of different infusions of coffee, &c., as a guide to its adulteration; and this is found in practice to work tolerably well, and to give approximative results. The following solutions were made by them by first treating the powder of the roasted substance with ten times its weight of cold water, boiling, and filtering, and determining the density at 60° Fahr.:—

Spent Tan,	1002·14
Lupine Seed,	1005·70
Acorns,	1007·30
Peas,	1007·30
Mocha Coffee,	1008·00
Beans,	1008·40
Neilgherry Coffee,	1008·40
Plantation Ceylon Coffee,	1008·70
Java Coffee,	1008·70
Jamaica Coffee,	1008·70
Costa Rica Coffee,	1009·00
,, ,,	1009·05
Native Ceylon Coffee,	1009·00
Brown Malt,	1010·90
Parsnips,	1014·30
Carrots,	1017·10
Bouka,	1018·50
Black Malt,	1021·20
Turnips,	1021·40
Rye-meal,	1021·60
Dandelion Root,	1021·90
Red-Beet,	1022·10
English Chicory,	1021·70
Yorkshire Chicory,	1019·10
Foreign Chicory,	1022·60
Guernsey Chicory,	1023·26
Mangel-Wurzel,	1023·50
Maize,	1025·30
Bread Raspings,	1026·30

When the microscope has detected chicory, and it is certain that nothing but chicory is present, the most reliable guide is the density of the infusion. Of the strength given, if the specific gravity of coffee infusion be taken as 1000·5 and that of chicory as 1022·0, then the following table, from the author's experiments, will be a fair guide to the amount of adulteration. The error usually lies within three per cent., while with regard to the soluble ash, the possible error is much higher. It hence follows that the analyst must be very careful in his statements as to the percentage of chicory. The certificate should say "*about . . . per cent.;*" or supposing that from the soluble ash and from the specific gravity, as well as from the microscopical examination, a coffee seems to contain 40 per cent. of chicory, it will be safe to subtract 5 per cent. for error, and give the amount as "*at least 35 per cent.*"

TABLE XXVIII., giving the Approximate Percentage of Chicory in a Decoction of Coffee and Chicory.

Specific gravity.	Percentage of Chicory in Mixture.	Specific gravity.	Percentage of Chicory in Mixture.	Specific gravity.	Percentage of Chicory in Mixture.	Specific gravity.	Percentage of Chicory in Mixture.
1009·0	3·74	1011·5	22·27	1014·0	40·74	1016·5	59·26
1009·1	4·39	1011·6	23·02	1014·1	41·49	1016·6	60·01
1009·2	5·14	1011·7	23·77	1014·2	42·24	1016·7	60·76
1009·3	5·89	1011·8	24·52	1014·3	42·99	1016·8	61·51
1009·4	6·64	1011·9	25·27	1014·4	43·74	1016·9	62·26
1009·5	7·39	1012·0	25·93	1014·5	44·49	1017·0	62·97
1009·6	8·14	1012·1	26·68	1014·6	45·24	1017·1	63·72
1009·7	8·89	1012·2	27·43	1014·7	45·99	1017·2	64·47
1009·8	9·64	1012·3	28·18	1014·8	46·74	1017·3	65·22
1009·9	10·39	1012·4	28·93	1014·9	47·49	1017·4	65·97
1010·0	11·12	1012·5	29·68	1015·0	48·15	1017·5	66·72
1010·1	11·87	1012·6	30·43	1015·1	48·90	1017·6	67·47
1010·2	12·62	1012·7	31·18	1015·2	49·65	1017·7	68·22
1010·3	13·37	1012·8	31·93	1015·3	50·40	1017·8	68·97
1010·4	14·12	1012·9	32·68	1015·4	51·15	1017·9	69·72
1010·5	14·87	1013·0	33·34	1015·5	51·90	1018·0	70·38
1010·6	15·62	1013·1	34·09	1015·6	52·65	1018·1	71·12
1010·7	16·37	1013·2	34·84	1015·7	53·40	1018·2	71·87
1010·8	17·12	1013·3	35·59	1015·8	54·15	1018·3	72·62
1010·9	17·87	1013·4	36·34	1015·9	54·90	1018·4	73·37
1011·0	18·52	1013·5	37·09	1016·0	55·65	1018·5	74·15
1011·1	19·27	1013·6	37·84	1016·1	56·40	1018·6	74·90
1011·2	20·02	1013·7	38·59	1016·2	57·15	1018·7	75·65
1011·3	20·77	1013·8	39·34	1016·3	57·90	1018·8	76·40
1011·4	21·52	1013·9	40·09	1016·4	58·65	1018·9	77·15
						1019·0	77·78

§ 215. W. L. Hiepe, taking into consideration the fact that pure coffee has ·03 per cent. of chlorine, while chicory has ·28 per cent. of chlorine, has proposed to calculate the percentage of mixtures on this data. If this method should be accepted, it will necessitate a most careful incineration; for in the majority of ordinary cases involving ash-taking, two-thirds of the chlorine is volatilised.

Prunier, again, has attempted to determine the coffee directly by weight: 2 grms. of the mixture of coffee and chicory are weighed out, and the finer powder is separated by sifting through fine silk. This is composed entirely of coffee, as may be proved by microscopic examination. That which remains on the silk sieve is moistened with water in a test glass; after some hours it is thrown upon a piece of stretched cloth, and crushed with the fingers. The grains of coffee resist the pressure, whilst those of chicory penetrate under these circumstances into the cloth, and adhere to it. The cloth is dried, and it is then easy to detach the coffee, which is added to the fine powder from the first operation, and weighed after complete drying; the chicory is calculated from the loss.

H. Hager's recent investigations into coffee adulteration may be detailed as follows:—To examine the unroasted coffee for artificial colouring-matters, he treats the berries with cold water; when, if the berries are in their natural state, the water is scarcely coloured. 50 grms. are next macerated with water, to which 1 per cent. of nitric acid has been added, and then hydric sulphide is passed through the filtrate; from this solution chloroform will extract indigo if present. Berlin-blue and alkanet pigment may be dissolved out from the berries by carbonate of potash solution, and then precipitated by hydrochloric acid. He finds also that when thrown into water, imitation or artificial berries will sink to the bottom, while good berries swim. On treating 3 grms. of powdered coffee with 20 grms. of cold water, and filtering, after the lapse of half an hour the filtrate should be feebly yellow, and not taste in the least degree bitter; in presence of lupin-seeds the taste is markedly bitter.

With regard to the "swimming test," he recommends a saturated solution of rock salt. 2 grms. of the coffee are placed in a narrow test cylinder with 15 to 20 cc. of the cold saline solution; the coffee is shaken up with this, and then allowed to stand for an hour; after this time the coffee swims to the surface, and the water remains uncoloured. Lupin-seeds generally colour the salt solution yellow, and give a strong deposit. The filtrate from pure coffee gives no precipitate with picric acid, tannin, iodine, or alkaline copper. Ferric chloride strikes

a green colour with false coffee; with starches iodine strikes a blue colour; with astringent matters, ferric chloride a black colour; if sugar from chicory, dates, &c., is present, alkaline copper solution is reduced.

Lupin-seeds give, when extracted by weak sulphuric acid water, only a slight turbidity with mercury potassic iodide. Coffee, on the contrary, under the same circumstances, gives a strong turbidity; but if this is doubtful, the theine can be extracted from the solution by shaking it with chloroform or benzole, which dissolves the theine, but leaves the lupin.

Hager has also a different method of taking the "extract:" 10 grms. of coffee, 1 grm. of oxalic acid, and 80 cc. of water are mixed by shaking, and digested at 100° for 3 hours, filtered, and washed with water until the filtrate is no longer coloured. The filtrate is evaporated to dryness. Pure coffee at the most yields in this manner 2·5 to 3 grms. of extract (including the oxalic acid), while chicory gives 5 to 7 grms., and other substances similarly much increase the extract. His reason for using oxalic acid is because of its changing starch into dextrine, and quickening the filtration.

§ 216. The seeds of *Cassia occidentalis* * are now being, to some extent, used as an adulterant, and as a substitute for coffee. In Germany the ground and roasted seeds have been sold under the name of "Mogdad" coffee, and it is said that neither by the taste nor by the general appearance can the addition of cassia seeds be detected, if such addition does not exceed one-fifth of the weight of the coffee. The seeds are small, flattened, oval, smooth, marked on each side of the two flattened surfaces with a slight circular groove or depression; when magnified the surface of the seed is somewhat tuberculated.

The integuments are wonderfully hard and leathery, and in the fresh state most difficult to grind or cut; they are, indeed, about the consistence of the leathery seeds of *Nux vomica*. The microscopical structure is very distinctive; the covering of the seed has first a layer of hard tissue, with fine striæ-like, perpendicular tubes radiating from the centre towards the circumference. These have a marked resemblance to the dentine of teeth, and may be appropriately called the dentine-like layer. There is a dark layer beneath the dentine layer, and this passes into some thick-walled four- to five-sided oblong cells, filled with an orange-red colouring-matter. Within the coloured cells are oval, round, or angular cells (according to the pressure),

* Holler: *J. Dingl. Pol. Journ.*, 237, p. 61; 238, p. 164.

filled with granular matter, and making up most of the substance of the seed (see fig. 40).*

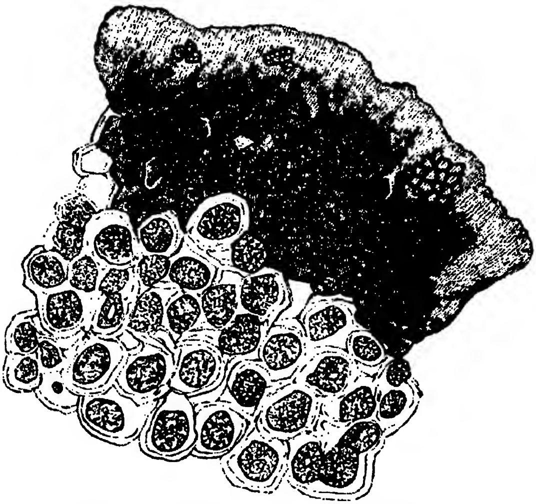

Fig. 40.—Section of Seed of *Cassia occidentalis*, × 170.

The composition of Mogdad coffee is as follows:—

Cellulose,	21·21
Fatty oil,	2·55
Plant mucus,	36·60
Astringent substance, gallo-tannic acid,	5·23
Inorganic salts,	4·33
Nitrogenous organic matters and loss,	15·13
Nitrogen-free organic matter,	3·86
Water,	11·09

§ 217. *Date Coffee.*—Recently there has been established a company for the manufacture of what is termed "Date coffee," a preparation made from torrified dates, and mixed with coffee, in the proportion of one-fourth coffee and three-fourths dates. A sample recently examined presented the appearance of a dark-brown, rather sticky powder, having a sweetish smell, but no coffee odour. On being thrown into water the water was immediately coloured, and the powder sank to the bottom. The specific gravity of the infusion was nearly that of pure chicory, viz., 1019·6. The microscope showed some fragments of coffee, as well as large loose cells and structures, quite different from

* The seeds of *Cassia occidentalis* give 10 per cent. of ash.

those of coffee, and there was scarcely a trace of theine. The general analysis gave :—

		Per cent.
Water,	. . . .	5·25
Sugar,	. . . .	15·29
Extract,	. . . .	46·50
Total ash,	{ Soluble, 1·87 / Insoluble, 1·07 }	2·85

The ash contained ·262 P_2O_5 and ·13 silica ; ·628 per cent. of an oily and resinous matter was also separated. The large amount of sugar would alone be sufficient to distinguish it from coffee, and there will not be the slightest difficulty in the identification of the substance should it be ever used in such a manner as to come under the Sale of Food and Drugs Act.

In regard to other adulterations, a great variety of starch-holding substances, with the cereals, may be entirely excluded, as certainly not present, if no dirty-blue or violet coloration is produced by iodine in an infusion of coffee. In order to apply this test properly, the infusion should be decolourised, which is most rapidly done by a solution of permanganate of potash. Coffee itself, as before stated, contains no starch.

Burnt sugar, or caramel, is usually detected by observing the rapid darkening of water on which a little coffee is sprinkled, and the particles (on examination in water by the microscope) reveal themselves by the absence of organised structure, and the coloured ring, arising from partial solution, round each.

BIBLIOGRAPHY.

ALLEN, A. H.—*Chem. News*, vol. xxix., 130, 140 : *Analyst*, Jan., 1880.

BOUCHARDAT.—"Falsification du Café."

CHEVALLIER.—Café indigène, *Ann. d'Hyg. et de Méd. Lég.*, 1853, t. xlix., p. 408 ; Sur l'enrobage des cafés, *Journ. Chim. Méd.*, 4e série, 1869, t. ix., p. 259 ; Du café, *Ann. d'Hyg. et de Méd. Lég.*, 2e série, 1862, t. xvij.

DESSAULT.—*Journ. Chim. Méd.*, 5e série, 1866, t. ii., p. 435.

DRAPER.—*Pharm. Journ.*, 3e série, t. ix., p. 142.

FRANZ, A.—*Arch. Pharm.* [5], 4, 298, 302.

GIRARDIN, J.—*Ann. d'Hyg. et de Méd. Lég.*, 1834, t. xi., p. 67 et p. 96.

HAGER, H.—*Zeitsch. Anal. Chem.*, vii. 388 ; xii. 232 ; xiii. 80 ; xv. 474.

HLASIWETZ.—*Ann. Chem. Pharm.*, cxlii. 219.

HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.

HUSSON, P.—Etude sur le Café, le Thé et les Chicorées. *Ann. de Chemie et de Physique*, 1879, 419.

HORSLEY.—*Pharm. Journ.*, 1855, t. xv.

LABICHE.—*Journ. Chim. Méd.*, 4e série, t. iv., 1858, p. 627.

LASSAIGNE, J. S.—*Journ. Chim. Méd.*, 3e serie, 1853, t. ix., p. 365.
LEPAGE.—*Journ. Chim. Méd.*, 3 série, 1853, t. ix., p. 618.
LEVESIE, O.—*Arch. Pharm.* [5], 4, p. 294.
ORMAN, V.—Falsification de café moulu avec la semence de ricin. *Journ. Chim. Méd.*, 3e série, 1852, t. viij., p. 50.
PFAFF.—*Schweigg's Journ.*, lxii. 31.
ROCHLEDER.—*Ann. Chem. Pharm.* 11, 300; lxiii. 193; lxi. 39; lxxxii. 194; *Journ. Pract. Chem.*, lxxii. 392; *Wien. Akad. Ber.*, xxiv. 46.
ROCHLEDER & HLASIWETZ.—*Ann. Chem. Pharm.*, lxxij. 338.
WANKLYN, J. A.—"Tea, Coffee, and Cocoa," Lond., 1876.

COCOA AND CHOCOLATE.

§. 218. The cocoa of commerce is made from the roasted seeds* of the *Theobroma cacao*, a tree belonging to the natural order *Byttneriaceæ*, whole forests of which exist in Demerara. It is also more or less extensively grown in Central America, Brazil, Peru, Caraccas, Venezuela, Ecuador, Grenada, Essequibo, Guayaquil, Surinam, and some of the West Indian Islands; and its cultivation has also been attempted (in most cases successfully) in the East Indies, Australia, the Philippine Islands, the Mauritius, Madagascar, and Bourbon.

The principal kinds of cocoa in commerce are known under the names of Caraccas, Surinam, Trinidad, Grenada, Jamaica, Dominica, Guayaquil, Venezuela, Bahia, Brazil, and St. Lucia. The seeds are officinal in the French and Norwegian pharmacopœias. They are ovate, flattened, 2 to 2½ cm. [·7 to ·9 inch] long, and 1 to 1½ cm. [·39 to ·58 inch] broad, and covered with a thin red or grey-brown friable shell. The taste of the fresh seed is oily, bitter, and rather unpleasant.

The seeds, on being submitted to a kind of fermentation (technically called the *sweating* process), lose in a great measure this disagreeable flavour, and develop an aromatic smell. Seeds which have been subjected to this treatment are best suited for the manufacture of chocolate, while those which have been simply roasted are richer in cocoa-butter.

§ 219. *Microscopical Structure of the Seed.*—The seed, when deprived of the husk, consists for the most part of several irregularly-shaped angular divisions, filled with a large number of oval cells, within which is contained a peculiar starch, as well as a fatty matter. Near the surface these cells are angular, and of a pronounced red colour, but the tint is somewhat variable.

The starch-granules are perfectly round, normal measurement

* The seeds simply dried are also sold.

about 0·52 mm. [·00021 inch], and are often seen to have a somewhat obscure starred hilum. They strike a pronounced blue colour with iodine.

The husk contains from without inwards the following structures :—

(1.) A superficial layer of large, very characteristic tubular fibres, containing granular matter and little corpuscles.

(2.) A single layer of elongated cells, with their greatest diameter transversely to the axis.

(3.) Large angular cells in several layers ; those in the centre mucilaginous, constituting the greatest bulk of the envelope.

(4.) A very delicate membrane, formed of small cells, enclosing fatty matters. This membrane adheres to the almond, and portions of it may always be seen in the chocolates of commerce.

Another hyaline and fibrous structure connected with the last, and full of crystals, is usually described, as well as isolated, dark, elongated bodies. The whole structure, therefore, is complex in a high degree, but familiarity with the appearance presented by the different portions of the seeds is readily obtained.

§ 220. The *commercial varieties of cocoa* are very numerous :—*Cocoa nibs* are simply the bruised, roasted seeds deprived of their coverings ; and *flake cocoa* is composed of the nibs ground in a particular form of mill. The soluble cocoas are—ground cocoa, diluted with sugar and starches—*e.g.*,

Epps's cocoa, according to an analysis advanced as evidence in the case of *Gibson* v. *Leafer*, is composed of cocoa 40 per cent., sugar 44 per cent., and starch 16 per cent.

Granulated cocoa is mostly a mixture of nibs, arrow-root, and sugar ; *Homœopathic cocoa*, a preparation of the same kind without the sugar ; *Maravilla cocoa* contains sugar and much sago flour ; and *cocoa essence*, *cocoatine*, &c., consist of pure cocoa deprived of 60 to 70 per cent. of its fat.

The above are examples only. The analyst is liable to meet any day with some new patent cocoa, for the consumption of this food is greatly on the increase.*

§ 221. *Chocolate.*—In the manufacture of chocolate the cocoa-nibs are ground in a mill, the rollers of which are usually heated by steam, so as to soften the cocoa-butter ; and in this way a paste is formed which is mixed with refined sugar, and very often other substances, and pressed into moulds. Some of the receipts for chocolate are as follows :—

* That the consumption of cocoa is increasing is evidenced by the quantity imported—in round numbers, 10,000,000 lbs. in 1876, against 9,000,000 lbs. in 1875.

(1.) *French Chocolate.*—2 beans of Vanilla rubbed into a powder with sugar, and 1 lb. of best sugar to every 3 lbs. of cocoa nibs.

(2.) *Spanish Chocolate.*—(*a.*) Curaçoa cocoa 11, sugar 3, Vanilla $\frac{1}{16}$, cinnamon $\frac{1}{64}$, cloves $\frac{1}{128}$. (*b.*) Caraccas cocoa 10, sweet almonds 1, sugar 3, Vanilla $\frac{1}{64}$.

Vanilla Chocolate.—A chocolate paste highly flavoured with Vanilla, and generally with other spices as well. (*a.*) Caraccas cocoa 7, Mexican Vanilla $\frac{1}{16}$, cinnamon $\frac{1}{32}$, and sufficient cloves to flavour. (*b.*) Best chocolate paste 21, Vanilla 4, cinnamon $\frac{1}{8}$, cloves and musk in small quantities.

The chocolates of English commerce yield but little cocoa-butter, since they are mostly prepared from the cake left after expression of the oil.

§ 222. The average chemical composition of cocoa, according to some English analyses, is as follows:—

	J. A. Wanklyn.	J. Muter.
Cocoa butter,	50·00	42·94
Theobromin,	1·50	·90
Starch,	10·00	19·03
Albumen, fibrine, and gluten,	18·00	12·21
Gum,	8·00	6·40
Colouring-matter,	2·60	3·69
Water,	6·00	5·98
Ash,	3·60	2·90
Loss, &c.,	0·30	...
Cellulose,	...	5·95
	100·00	

The peculiar constituents of cocoa are then two—viz., cocoa-butter and theobromin.

Cocoa-butter, Oleum theobromæ, specific gravity, 0·96 to 0·98;* melting point, 29° to 30°; solidifying point, 24°, is a yellowish-white, concrete oil about the consistency of tallow, with a chocolate colour and an agreeable taste. At common temperatures it is brittle, the fracture is smooth and equal, and examined by a lens it is somewhat crystalline. It is fully soluble at ordinary temperatures in two parts of ether, in half a part of benzole, as well as in 100 parts of cold and 20 parts of hot absolute alcohol; its solution is entirely neutral to test paper. If adulterated with tallow, wax, paraffin, or stearin, the specific gravity will be altered, and it will not dissolve to a clear solution in the quantity of ether named above. Pure cocoa butter does not become rancid, however long it is kept; but the admixture of most

* Its specific gravity was formerly given as from ·89 to ·91; but Flückiger, as well as Hirsch, has shown that this is too low.

foreign fats impairs this property. Cocoa-butter is usually said to consist of cocoa stearin, which separates in warty masses on evaporating an ethereal solution, and has a melting point of 65° with a little olein. Kingzett has, however, recently described two new fatty acids obtained from cocoa fat, one of which has the empiric formula $C_{64}H_{128}O_2$, and the subject appears to require further research. The best method of extracting the fat is to exhaust the nibs with ether in the apparatus figured at page 67.

Cocoa should contain at least 20 per cent. of cocoa fat; if less than that is found, it should be returned as adulterated.*

§ 223. *Theobromin*, $C_7H_8N_4O_2$.—This alkaloid was discovered in 1841 by Woskresensky, in the seeds of the *Theobroma cacao;* it principally resides in the cotyledons, and in smaller quantities in the seed-coverings. The average yield of theobromin appears to be $1\frac{1}{2}$ per cent.

The original method of separation pursued by Woskresensky was—extraction on the water-bath with distilled water, filtering through linen, precipitating with sugar of lead, refiltering, freeing the filtrate from excess of lead by SH_2, evaporating to dryness, and subsequent purifying of the residue by solution in spirit, and treatment with animal charcoal. Mitscherlich, again, boils the cocoa with a weak solution of sulphuric acid in order to change the starch into sugar, saturates the fluid with carbonate of lead, and ferments it with yeast to destroy the sugar. On the conclusion of the fermentation, the fluid is boiled, neutralised with soda, filtered, concentrated by evaporation, and the impure brown theobromin which separates boiled in hot nitric acid. This nitric acid solution is precipitated by ammonia, again dissolved in nitric acid, and the nitrate obtained by evaporation. According to Mitscherlich, the quantity obtained in this way is much greater than by other processes.

A speedy method of determining, with very fair exactitude, the percentage of theobromin in cocoa, is to exhaust a weighed quantity with petroleum ether, mix the residue with a little burnt magnesia and water, evaporate to dryness at 60° to 70°, and then exhaust the residue with boiling alcohol of 80 per cent., which dissolves out the theobromin. On driving off the alcohol by evaporation, the substance may be purified sufficiently for weighing purposes by washing with petroleum ether.

G. Wolfram has recommended the following process for the extraction of theobromin:—10 grms. of the substance are

* 20 per cent. is the standard of the Society of Analysts; but in the writer's opinion this is much too low, according to published analyses.

powdered and exhausted with hot water, filtered, and the filtrate precipitated by ammoniacal acetate of lead, and the precipitate washed with boiling water, until the filtrate, acidified by sulphuric acid, no longer gives a precipitate with phospho-tungstic acid. The filtrate is made alkaline by soda, evaporated to 50 cc., strongly acidified by sulphuric acid, and the lead sulphate filtered off. The filtrate is now precipitated by a large excess of sodium phospho-tungstate, and the precipitate decomposed by hot baryta water; the barium phospho-tungstate is filtered off, and the filtrate freed from baryta by adding sulphuric acid in very slight excess, the excess being got rid off by adding a little barium carbonate. The alkaloid is obtained by filtration, and evaporating the first filtrate to dryness, weighing, and then igniting, and again weighing—the difference equals the alkaloid. The ignition is necessary, for there is always a little baryta which has not been got rid of by the previous operations. In six analyses of various cocoas, Wolfram obtained as a maximum, 1·66 per cent.; as a minimum, 1·34 per cent.; and as a mean, 1·56 per cent. of theobromin, in the dried cocoa-beans divested of their coverings; while the dried husk of the six cocoas contained maximum 1·11, minimum ·42, mean ·76 per cent. theobromin.

Theobromin forms microscopic rhombic needles. It is generally thought to sublime between 296° and 295° without decomposition, but this temperature is many degrees too high. The writer finds that a minute fragment, placed in the subliming cell elsewhere described, begins to give fine nebulæ at 134°, and on examining the mists by a high power, they are resolved into extremely minute dots; distinct crystals are obtained at temperatures of 170° and above. Theobromin is insoluble in petroleum ether, and not very soluble in ether, 1 part requiring 600 parts of boiling and 1,700 parts of cold ether. It is soluble in alcohol, 1 part requiring 47 parts of boiling and 1,460 of cold alcohol. Its solubility in water is stated to be 1 in 55 parts at 100°, 1 in 600 parts at 20°, and 1 in 1,600 at 0°. It is somewhat soluble in chloroform and warm amyl-alcohol, but with difficulty soluble in benzole.

Theobromin forms easily crystallisable salts. The simple neutral salts are decomposed by water, with the formation of basic salts, and lose their acid, if it is volatile, at 100°. A hydrochloride of theobromin, $C_7H_8N_4O_2,HCl$; a nitrate, $C_7H_8N_4O_2,NHO_3$; a platinum salt, $C_7H_8N_4O_2,HClPtCl_2 + 2H_2O$; are all very definite crystalline compounds. A noteworthy salt is the nitrate of silver, which is formed by adding a solution of argentic nitrate to a solution of nitrate of theobromin; in a short

time there separate silver-white needles, very insoluble in water, of the composition $C_7H_8N_4O_2,NHO_3 + AgNO_3$.

The other precipitants of theobromin are—phospho-molybdic acid (yellow) and chloride of gold (long needles). Tannic and picric acids only produce turbidity, while potass. mercuric iodide and potass. cadmium iodide do not precipitate. A characteristic reaction of theobromin is that produced by peroxide of lead and sulphuric acid. If peroxide of lead and diluted sulphuric acid are heated with theobromin, avoiding an excess of the oxidising agent, CO_2 is developed, and the colourless filtrate of sulphate of lead gives off ammonia with potash, separates sulphur on treatment with SH_2, stains the skin purple-red, and colours magnesia indigo-blue.

Theobromin is poisonous to kittens (and other animals of similar size) in such large doses as a gramme. It appears to be separated by the kidneys, and could probably be discovered in the urine of any person taking large quantities of cocoa. The method of research successfully used by Mitscherlich is as follows:—The urine is acidified with HCl, filtered, and to the filtrate, acidified with nitric acid, a solution of phospho-molybdate of soda is added. The precipitate is collected, and treated with baryta water until it is strongly alkaline, warmed, filtered, and the filtrate evaporated; the residue extracted with alcohol, re-filtered, and the filtrate again evaporated. This last residue is dissolved in a drop of hydrochloric acid, and precipitated by ammonia. The alkaloid may now be collected and, if necessary, purified.

§ 224. *The Ash.*—The composition of the ash of cocoa seeds is stated by Mr. Wanklyn to be as follows:—

COMPOSITION OF ASH OF COCOA-SEEDS.

	Per cent.
Potash,	29·81
Chloride of Sodium,	6·10
Ferrous Oxide,	1·60
Alumina,	2·40
Lime,	7·72
Magnesia,	7·90
Phosphoric Acid,	24·28
Sulphuric Acid,	1·92
Carbonic Acid,	0·98
Silica,	5·00
Sand,	12·15

The percentages of ash found in cocoa are given as follows:—

	Percentage of Ash.
Common Trinidad, ...	3·37
Very fine Trinidad, ...	3·62
Fair, good, fine Trinidad, ...	3·64
Fine Grenada, ...	3·06
Caraccas, ...	4·58
Bahia (Brazil), ...	3·31
Fine Surinam (small), ...	3·06
Mexican, ...	4·27
Dominican, ...	2·82
African, ...	2·68
Mean of the twelve being	3·39

Thus the lowest determination is 3·06, the highest 4·58 per cent. The nibs show a lower ash than the shell. The nibs of the Caraccas give 3·95 per cent. of ash, 2·00 being soluble and 1·95 insoluble in water. The nibs of Mexican seeds give 2·59 per cent. of ash, ·89 parts being soluble and 1·70 insoluble in water. The ash of the shell is rich in, but the nib almost devoid of, carbonates. Mr. Heisch has also recently examined the cocoas of commerce, with the results embodied in the following tables:—

TABLE XXIX.—EXAMINATION OF ROASTED BEANS AFTER REMOVAL OF THE HUSK.

	Husk.	Fat.	Nitrogen.	Albuminoids.	Ash.	Ash Soluble in Water.	Ash Soluble in HCl.	H_3PO_4 in Ash.	Moisture.	Starch, Gum, Cellulose, &c.
Caraccas, .	13·8	48·4	1·76	11·14	3·95	2·15	1·80	1·54	4·32	32·19
Trinidad, .	15·5	49·4	1·76	11·14	2·80	0·90	1·90	0·93	3·84	32·82
Surinam, .	15·5	54·4	1·76	11·14	2·35	0·80	1·85	1·23	3·76	28·35
Guayaquil,	11·5	49·8	2·06	13·03	2·50	1·75	1·75	1·87	4·14	30·47
Grenada, .	14·6	45·6	1·96	12·40	2·40	0·60	1·80	1·35	3·90	35·70
Bahia, . .	9·6	50·3	1·17	7·40	2·60	0·90	1·70	1·26	4·40	35·30
Cuba, . .	12·0	45·3	1·37	8·67	2·90	0·95	1·95	1·13	3·72	39·41
Para, . .	8·5	54·0	2·00	12·66	3·05	1·40	1·65	1·00	3·96	26·33

The above analyses fully corroborate Mr. Wanklyn's statement as to the constancy of the percentage of phosphoric acid in cocoa ash. Mr. Heisch's highest determinate is 1·87, his lowest ·93, giving a mean of 1·28 per cent. phosphoric acid in the dry bean after removal of the husk.

There are also some analyses by König as follows:—

TABLE XXX.

I. COCOA BEANS DEPRIVED OF THE SHELL.

	Water.	Nitrogenous Substances.	Fat.	Starch.	Other Nitrogen free Matters.	Cellulose.	Ash.
1. Caraccas I., . .	4·04	14·68	46·18	12·74	(18·50)	...	3·86
2. ,, II., . .	4·72	14·06	49·36	13·99	9·46	4·20	4·21
3. Guayaquil I., .	3·63	14·68	49·64	11·56	12·64	4·13	3·72
4. ,, II., .	2·61	16·25	46·99	10·82	16·12	3·53	3·68
5. Trinidad I., . .	2·81	15·06	48·32	14·91	12·06	3·62	3·22
6. ,, II., . .	2·28	15·12	52·14	14·38	8·82	3·87	3·39
7. Puerto Cabello, .	2·96	15·03	50·57	12·94	11·49	3·07	3·94
8. Socosnusco, . .	2·95	13·19	48·38	15·13	13·20	3·34	3·21
Mean, . . .	3·25	14·76	49·00	13·31	12·35	3·68	3·65

II. COCOA HUSKS.

	Amount of Shell.	Water.	Nitrogenous Substances.	Fat.	Nitrogen Free Constituent.	Cellulose.	Ash.	Sand.
1. Caraccas I., .	15.03	7·41	13·93	4·94	41·78	12·91	7·41	12·62
2. ,, II.,.	20·09	7·74	11·68	5·99	35·29	12·79	8·32	18·19
3. Guayaquil, .	...	8·93	13·44	8·12	48·01	13·87	6·81	0·82
4. ,, .	...	9·11	12·94	10·75	47·08	13·12	6·79	0·21
5. Trinidad, .	15·35	9·04	14·94	6·18	44·80	16·36	6·39	2·29
6. ,, .	14·04	8·30	15·44	4·23	46·05	18·00	7·06	0·92
7. Puerto Cabello,	14·92	6·40	13·75	4·38	47·12	14·83	6·06	7·46
8. Socosnusco, .	18·58	6·48	19·12	6·48	39·39	15·67	8·15	4·71
Mean, . .	16·33	7·83	14·29	6·38	43·79	14·69	7·12	5·90

§ 225. Mr. Wigner has examined the nitrogenous constituents of cocoa, in the same way as the nitrogenous constituents of flour, and has shown that, even in the very best samples, 21·5 per cent. of the nitrogenous matter present is in a non-coagulable form. Cocoa, therefore, ranks lower in the scale of foods than has hitherto been taught. His experiments were made upon 84 commercial samples of cocoa, containing an admixture of starch or flour, and on four samples of roasted beans; the results were as follows:—

TABLE XXXI.—NITROGENOUS CONSTITUENTS OF COCOA.

	Total Nitrogen.	Coagulable Nitrogen.	Total Albuminoids = N × 6·33.	Coagulable Albuminoids = N × 6·33.	Difference = Non-Coagulable Nitrogen Matter.	Per cent. Total Non-Coagulable
1.	1·095	·600	9·92	3·80	3·12	54·9
2.	1·162	·760	7·35	4·81	2·54	65·5
3.	2·978	2·335	18·84	14·79	4·05	78·5
4.	·965	·375	6·11	2·37	3·74	38·8
5.	·699	·330	4·42	2·09	2·33	47·3
6.	1·201	·770	7·61	4·88	2·73	34·1
Roasted beans, Socunza,	2·040	1·175	12·92	7·44	4·48	57·6
Roasted beans, Para,	2·000	1·045	12·67	6·62	6·05	52·2
Roasted beans, Trinidad,	1·490	1·050	9·46	6·65	2·81	70·3
Roasted beans, Grenada,	2·370	1·335	14·99	7·56	7·43	50·4

§ 226. *Adulterations of Cocoa.*—The list of adulterations usually given is as follows:—Sugar, starches, Venetian red, brick-dust, and peroxide of iron. Some of these sophistications, such as the starches, may be detected by a preliminary microscopical examination, which in no instance should be neglected. The ordinary chemical examination consists in the extraction of the fat as before described (p. 361), the estimation of the percentage of ash in the ordinary way, its division into soluble and insoluble, and its content of phosphoric acid. By a simple estimation of the fat and the chief constituents of the ash, supplemented by the use of the microscope, all known adulterations can be detected. The amount of phosphoric acid in the ash of soluble cocoas may be taken as a basis of calculation of the amount of cocoa, and in the absence of foreign seeds, or other phosphate-producing substance, the calculation will be a fair approximation to the truth. The ash itself and the amount of phosphoric acid will, of course, be very notably diminished in the case of the soluble cocoas, and the percentage of the phosphoric acid will in such instances be a fair guide to the amount of foreign admixture. For example, suppose a soluble cocoa to yield an ash of 1·5 per cent., ·6 of which is due to phosphoric acid, taking as a basis of calculation ·9 per cent.* of phosphoric acid in cocoa nibs:—

* The lowest percentage given by Mr. Heisch, and but little different from Mr. Wanklyn's.

$$\frac{\cdot 6 \times 100}{\cdot 9} = 66 \cdot 6$$

That is, the mixture contains about 66·6 per cent. of cocoa. The amount of starch in cocoa may be determined in the ordinary way, as described at p. 137, but the process is somewhat tedious, and may be dispensed with, since the extract in cold water is always a guide to the adulteration by starchy substances. Cocoa nibs treated in this way give to water about 6·76 per cent. of organic matter and 2·16 of ash. The determination of theobromin may possibly be of use, but no sufficiently accurate and speedy process for technical purposes is as yet known.

§ 227. *Adulterations of Chocolate.*—Oil of almonds, cocoa-oil, beef and mutton fat, starches, cinnabar, chalk, and various other substances are usually enumerated; a few of these are, however, apocryphal.

The analysis of chocolate is conducted on exactly the same principles as that of soluble cocoa. If it is desired to separate the different constituents, the method recommended by A. Porrier may be used:—Extract the fat with ether, and the sugar with alcohol of 20°, and dissolve the starch out by boiling water. The liquid holding the starch is then decolourised by animal charcoal, and the starch precipitated by alcohol of 50 per cent., dried, and weighed. But as regards adulteration, the procedure recommended in the case of cocoa will be found quite efficient, and less cumbersome and tedious.

BIBLIOGRAPHY.

Barbet.—Procédé pour reconnaître la quantité de fécule contenue dans les chocolats. *Journ. Chim. Méd.*, 4e série, 1857, t. iii., p. 121.

Bjorkland.—Moyen de reconnaître la falsification du beurre de cacao, &c. *Journ. Chim. Méd.*, 3 série, 1869, t. v., p. 147.

Briois.—Essai sur la recherche et le dosage de la fécule dans le chocolat. *Journ. Chim. Méd.*, 4e série, 1856, t. ii., p. 497.

Chevallier.—Mémoire sur le chocolat, sa préparation, ses usages, les falsifications qu'on lui fait subir, les moyens de les reconnaître. *Ann. d'Hyg. et de Méd. Lég.*, 2e série, 1846, t. xxxvj., p. 241; ib., *Journal d'Hyg.*, 28, 1876.

Cooley's "Dictionary of Practical Receipts." Arts., Chocolate and Cocoa.

Glasson.—*Ann. Chem. Pharm.*, lx. 335.

Girardin et Bidard.—Sur la fécule de cacao. *Journ. Pharm. et Chim.*, 2e série, 1852, t. xxxvij., p. 266.

HEISCH.—On the Composition of Different Kinds of Cocoa. *Analyst*, i., 1877, p. 142.
HIRSCH.—"Die Prüfung der Arzneimittel."
HUSEMANN.—"Die Pflanzenstoffe."
KELLER.—*Ann. Chem. Pharm.*, lx. 335.
KINGZETT, C. T.—The Chemistry of Cocoa Butter. *Journ. Chem. Soc.*, 1878, p. 42.
LETELLIER.—Falsification des chocolats. *Journ. de Pharm. et Chim.*, 3e série, 1854, t. xxv., p. 362.
MITSCHERLICH, A.—"Der Cacao und die Chocolade." 1859.
MUTER, JOHN.—On "Prepared" Cocoa. *Analyst*, 1879, p. 65.
PORRIER.—Sur le dosage des matières amylacées ajoutées frauduleusement au chocolat. *Journ. Chim. Méd.*, 2e série, 1858, t. ix., p., 297.
STRECKER.—*Ann. Chem. Pharm.*, cxviij. 151.
WANKLYN.—"Tea, Coffee, and Cocoa." Lond., 1876.
WIGNER, G. W.—On the Nitrogenous Constituents of Cocoa. *Analyst*, 1879, p. 8.
WOLFRAM, G.—*Zeitschrift f. Anal. Chem.*, 1879, s. 346.
WOSKRESENSKY.—*Ann. Chem. Pharm.*, xli. 125.

PART VI.—ALCOHOL, SPIRITS, LIQUEURS.

ALCOHOL.

§ 228. The term *alcohol,* in its strict chemical sense, applies only to the neutral compounds of oxygen, carbon, and hydrogen, which, by the action of acids, form ethers. The principal alcohols are enumerated in the following table:—

TABLE XXXII., EXHIBITING THE PROPERTIES OF THE PRINCIPAL ALCOHOLS.

Alcohols.	Formula.	Specific Gravity, 15·5°.		Vapour. Rel. Wt. H=1.	Boiling Point.	
		Liquid.	Vapour.		Fahr.	Cent.
1. Wood Spirit, or Methylic Alcohol,	CH_4O	0·798	1·12	16	149·9	65·5
2. Spirit of Wine, or Ethylic Alcohol,	C_2H_6O	0·7938	1·6133	23	173·0	78·3
3. Tritrylic or Propylic, . . .	C_3H_8O	0·817	2·02	30	206·0	96·7
4. Tetrylic or Butylic,	$C_3H_{10}O$	0·8032	2·589	37	233·0	111·7
5. Fousel Oil, or Amylic, . . .	$C_5H_{12}O$	0·8184	3·147	44	269·6	132·0
6. Hexylic or Caproic,	$C_6H_{14}O$	0·833	3·53	51	299-309	138-154
7. Heptylic, . .	$C_7H_{16}O$	0·819	...	58	351·0	177·2
8. Octylic or Caprylic,	$C_8H_{18}O$	0·823	4·50	65	356·0	180·0
10. Laurylic, . .	$C_{12}H_{26}O$	...	...	...	...	...
16. Ethal or Cetylic, .	$C_{16}H_{34}O$	...	...	...	...	...
27. Cerotin or Cerylic,	$C_{27}H_{56}O$	...	...	...	...	...
50. Melissin or Melisylic, . .	$C_{30}H_{62}O$	...	...	...	...	...

Of these ethylic alcohol, wood spirit, and fousel oil are the three of most importance to the analyst.

Ethylic Alcohol, C_2H_6O, specific gravity, 0·815 at 0°, 0·79381 at 15·5°; boiling-point, 78°·3. Absolute alcohol does not dissolve common salt, nor does it give a blue colour when digested with anhydrous sulphate of copper, if perfectly water-free. Filter paper saturated in the following solution—viz., two parts of

citric and one of molybdic acids heated to incipient fusion, and dissolved in 30 to 40 pints of water and dried at 100°, is not bleached when soaked in absolute alcohol; but should water be present, the blue of the paper is entirely discharged. Pure absolute alcohol burns with a white flame, but if water is present with a blue.

There is no cloudy appearance when mixed with water, showing the absence of oily matters. It should be also perfectly neutral to test paper, and leave no residue on evaporation. It must be remembered that, in a commercial sense, "absolute alcohol" is any stronger spirit than can be obtained by ordinary distillation; and, since this is the case, it would be most unwise for any action to be taken under the "Sale of Food and Drugs Act," unless a distinctly fraudulent statement has been made. "Absolute alcohol," as bought over the counters of the chemist, is seldom above from 93 to 95 per cent.

§ 229. *Rectified Spirit,* as defined by our own pharmacopœia, should be of specific gravity 0·838; by that of the Netherlands 0·830 to 0·834; of Germany, Switzerland, and Norway, 0·8336; of Austria, 0·838; of France, 0·835 to 0·841. It should be neutral, colourless, volatilising without residue, and free from other alcohols.

Proof Spirit,—a term in constant use for purposes of excise,—is a diluted spirit, which was defined by Act of Parliament (58 George III.) to be "such as shall, at the temperature of 10°·0 [51° Fahr.] weigh exactly twelve-thirteenth parts of an equal measure of distilled water." According to Drinkwater it consists of—

Alcohol by weight, ...	49·24
Water by weight, ...	50·76
	100·00

and its specific gravity at 15°·5 is 0·91984.

In the analysis of all spirits (seeing that the terms "proof" and "under proof" are used and known in the trade), the statements of results should always include the percentage of proof spirit.

Spirits weaker than proof are described as U.P., under proof; stronger than proof as O.P., over proof; thus a spirit of 50 U.P. means 50 water and 50 proof spirit, 60 U.P., 60 water and 40 proof spirit. On the other hand, 50 O.P. means that the alcohol is of such a strength, that, to every 100 of the spirit, 50 of water would have to be added to reduce it to proof strength. In all the above the strengths are only good for the normal temperature of 15°·5.

TABLE XXXIII.—ESTIMATION OF ALCOHOL.

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
1.0000	0·00	0·00	0·00	·9549	31·69	38·11	66·80
·9999	0·05	0·07	0·12	·9539	32·31	38·82	68·04
·9989	0·58	0·73	1·28	·9529	32·94	39·54	69·29
·9979	1·12	1·42	2·48	·9519	33·53	40·20	70·46
·9969	1·75	2·20	3·85	·9509	34·10	40·84	71·58
·9959	2·33	2·93	5·13	·9499	34·57	41·37	72·50
·9949	2·89	3·62	6·34	·9489	35·05	41·90	73·43
·9939	3·47	4·34	7·61	·9479	35·55	42·45	74·39
·9929	4·06	5·08	8·90	·9469	36·06	43·01	75·37
·9919	4·69	5·86	10·26	·9459	36·61	43·63	76·45
·9909	5·31	6·63	11·62	·9449	37·17	44·24	77·53
·9899	5·94	7·40	12·97	·9439	37·72	44·86	78·61
·9889	6·64	8·27	14·50	·9429	38·28	45·47	79·68
·9879	7·33	9·13	15·99	·9419	38·83	46·08	80·75
·9869	8·00	9·95	17·43	·9409	39·35	46·64	81·74
·9859	8·71	10·82	18·96	·9399	39·85	47·18	82·69
·9849	9·43	11·70	20·50	·9389	40·35	47·72	83·64
·9839	10·15	12·58	22·06	·9379	40·85	48·26	84·58
·9829	10·92	13·52	23·70	·9369	41·35	48·80	85·53
·9819	11·69	14·46	25·34	·9359	41·85	49·34	86·47
·9809	12·46	15·40	26·99	·9349	42·33	49·86	87·37
·9799	13·23	16·33	28·62	·9339	42·81	50·37	88·26
·9789	14·00	17·26	30·26	·9329	43·29	50·87	89·15
·9779	14·91	18·36	32·19	·9319	43·76	51·38	90·03
·9769	15·75	19·39	33·96	·9309	44·23	51·87	90·89
·9759	16·54	20·33	35·63	·9299	44·68	52·34	91·73
·9749	17·33	21·29	37·30	·9289	45·14	52·82	92·56
·9739	18·15	22·27	39·03	·9279	45·59	53·29	93·39
·9729	18·92	23·19	40·64	·9269	46·05	53·77	94·22
·9719	19·75	24·18	42·38	·9259	46·50	54·24	95·05
·9709	20·58	25·17	44·12	·9249	46·96	54·71	95·88
·9699	21·38	26·13	45·79	·9239	47·41	55·18	96·70
·9689	22·15	27·04	47·39	·9229	47·86	55·65	97·52
·9679	22·92	27·95	48·98	·9219	48·32	56·11	98·34
·9669	23·69	28·86	50·57	·9209	48·77	56·58	99·16
·9659	24·46	29·76	52·16	·9199	49·20	57·02	99·93
·9649	25·21	30·65	53·71	·9198	49·24	57·06	100·00 PS.
·9639	25·93	31·48	55·18				
·9629	26·60	32·27	56·55	·9189	49·68	57·49	100·76
·9619	27·29	33·06	57·94	·9179	50·13	57·97	101·59
·9609	28·00	33·89	59·40	·9169	50·57	58·41	102·35
·9599	28·62	34·61	60·66	·9150	51·00	58·85	103·12
·9589	29·27	35·35	61·95	·9149	51·42	59·26	103·85
·9579	29·93	36·12	63·30	·9139	51·83	59·68	104·58
·9569	30·50	36·76	64·43	·9129	52·27	60·12	105·35
·9559	31·06	37·41	65·55	·9119	52·73	60·56	106·15

TABLE XXXIII.—*Continued.*

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
·9109	53·17	61·02	106·93	·8649	73·00	79·54	139·39
·9099	53·61	61·45	107·69	·8639	73·42	79·90	140·02
·9089	54·05	61·88	108·45	·8629	73·83	80·26	140·65
·9079	54·52	62·36	109·28	·8619	74·27	80·64	141·33
·9069	55·00	62·84	110·12	·8609	74·73	81·04	142·03
·9059	55·45	63·28	110·92	·8599	75·18	81·44	142·73
·9049	55·91	63·73	111·71	·8589	75·64	81·84	143·42
·9039	56·36	64·18	112·49	·8579	76·08	82·23	144·10
·9029	56·82	64·63	113·26	·8569	76·50	82·58	144·72
·9019	57·25	65·05	113·99	·8559	76·92	82·93	145·34
·9009	57·67	65·45	114·69	·8549	77·33	83·28	145·96
·8999	58·09	65·85	115·41	·8539	77·75	83·64	146·57
·8989	58·55	66·29	116·18	·8529	78·16	83·98	147·17
·8979	59·00	66·74	116·96	·8519	78·56	84·31	147·75
·8969	59·43	67·15	117·68	·8509	78·96	84·64	148·32
·8959	59·87	67·57	118·41	·8499	79·36	84·97	148·90
·8949	60·29	67·97	119·12	·8489	79·76	85·29	149·44
·8939	60·71	68·36	119·80	·8479	80·17	85·63	150·06
·8929	61·13	68·76	120·49	·8469	80·58	85·97	150·67
·8919	61·54	69·15	121·18	·8459	81·00	86·32	151·27
·8909	61·96	69·54	121·86	·8449	81·40	86·64	151·83
·8899	62·41	69·96	122·61	·8439	81·80	86·96	152·40
·8889	62·86	70·40	123·36	·8429	82·19	87·27	152·95
·8879	63·30	70·81	124·09	·8419	82·58	87·58	153·48
·8869	63·74	71·22	124·80	·8409	82·96	87·88	154·01
·8859	64·17	71·62	125·51	·8399	83·35	88·19	154·54
·8849	64·61	72·02	126·22	·8389	83·73	88·49	155·07
·8839	65·04	72·42	126·92	·8379	84·12	88·79	155·61
·8829	65·46	72·80	127·59	·8369	84·52	89·11	156·16
·8819	65·88	73·19	128·25	·8359	84·92	89·42	156·71
·8809	66·30	73·57	128·94	·8349	85·31	89·72	157·24
·8799	66·74	73·97	129·64	·8339	85·69	90·02	157·76
·8789	67·17	74·37	130·33	·8329	86·08	90·32	158·28
·8779	67·58	74·74	130·98	·8319	86·46	90·61	158·79
·8769	68·00	75·12	131·64	·8309	86·85	90·90	159·31
·8759	68·42	75·49	132·30	·8299	87·23	91·20	159·82
·8749	68·83	75·87	132·95	·8289	87·62	91·49	160·33
·8739	69·25	76·24	133·60	·8279	88·00	91·78	160·84
·8729	69·67	76·61	134·25	·8269	88·40	92·08	161·37
·8719	70·08	76·98	134·90	·8259	88·80	92·39	161·91
·8709	70·48	77·32	135·51	·8249	89·19	92·68	162·43
·8699	70·88	77·67	136·13	·8239	89·58	92·97	162·93
·8689	71·29	78·04	136·76	·8229	89·96	93·26	163·43
·8679	71·71	78·40	137·40	·8219	90·32	93·52	163·88
·8669	72·13	78·77	138·05	·8209	90·68	93·77	164·33
·8659	72·57	79·16	138·72	·8199	91·04	94·03	164·78

TABLE XXXIII.—*Continued.*

Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.	Specific gravity, 15·5°.	Absolute Alcohol by weight. Per cent.	Absolute Alcohol by volume. Per cent.	Proof Spirit. Per cent.
·8189	91·39	94·28	165·23	·8039	96·73	97·96	171·68
·8179	91·75	94·53	165·67	·8029	97·07	98·18	172·05
·8169	92·11	94·79	166·12	·8019	97·40	98·39	172·43
·8159	92·48	95·06	166·58	·8009	97·73	98·61	172·80
·8149	92·85	95·32	167·04	·7999	98·06	98·82	173·17
·8139	93·22	95·58	167·50	·7989	98·37	99·00	173·50
·8129	93·59	95·84	167·96	·7979	98·69	99·18	173·84
·8119	93·96	96·11	168·24	·7969	99·00	99·37	174·17
·8109	94·31	96·34	168·84	·7959	99·32	99·57	174·52
·8099	94·66	96·57	169·24	·7949	99·65	99·77	174·87
·8089	95·00	96·80	169·65	·7939	99·97	99·98	175·22
·8079	95·36	97·05	170·07				
·8069	95·71	97·29	170·50	Absolute Alcohol.			
·8059	96·07	97·53	170·99				
·8049	96·40	97·75	171·30	·7938	100·00	100·00	175·25

ESTIMATION OF ALCOHOL

§230. Excellent tables for the use of analysts have been published both by Mr. Hehner and by Dr. Stevenson. The table on p. 371 will be found, in the absence of the tables mentioned, sufficient for ordinary use; any specific gravity not given can be intercalated by the ordinary rules of arithmetic.

Another method, sometimes called Gröning's, of arriving at the strength of dilute spirits, is based on the fact that the temperature of the vapour is an exact measure of the strength of the alcohol. The bulb of a thermometer is put (on the small scale) into a flask with a bilateral tube, and the temperature of the vapour carefully noted. The following table (XXXIV.) may be used.

The boiling-point is also a useful guide; for within certain limits the boiling-point of alcoholic liquids is not materially altered by admixture with saline and organic matter. A thermometer with a movable scale is employed. Before using it, the thermometer is immersed in boiling distilled water, and the 100° [212° Fahr.] of the scale accurately adjusted to the level of the mercury; it is then ready for an operation of several hours, or even an entire day, if no considerable variations of atmospheric pressure are experienced.

TABLE XXXIV., SHOWING THE ALCOHOLIC CONTENT BY VOLUME OF BOILING SPIRITS AND OF THEIR VAPOUR, FROM THE TEMPERATURE OF THE LATTER, AS OBSERVED BY A THERMOMETER. BY GRÖNING.

Temperature of the Vapour (F.)	Alcoholic Content of the Distillate. Per cent.	Alcoholic Content of the Boiling Liquid. Per cent.	Temperature of the Vapour (F.)	Alcoholic Content of the Distillate. Per cent.	Alcoholic Content of the Boiling Liquid. Per cent.
170·0	93	92	189·8	71	20
171·8	92	90	192·0	68	18
172·0	91	85	194·0	66	15
172·8	90½	80	196·4	61	12
174·0	90	75	198·6	55	10
174·6	89	70	201·0	50	7
176·0	87	65	203·0	42	5
178·3	85	50	205·4	36	3
180·8	82	40	207·7	28	2
183·0	80	35	210·0	13	1
185·0	78	30	212·0	0	0
187·4	76	25			

TABLE XXXV., EXHIBITING THE BOILING POINTS OF ALCOHOL AND WATER OF THE GIVEN STRENGTHS. BY GRÖNING.

Boiling-point (F.)	Alcohol per cent. per Volume.	Boiling-point (F.)	Alcohol per cent. per Volume.
205·34	5	179·96	55
199·22	10	179·42	60
195·80	15	178·70	65
192·38	20	177·62	70
189·50	25	176·54	75
187·16	30	175·46	80
185·00	35	174·92	85
183·38	40	174·20	90
182·12	45	173·14	95
181·58	50	172·00	100

§ 231. *Tests for Alcohol.*—The principal tests for alcohol are the following :—

(1.) *Production of Acetic Ether.*—To a distillate or aqueous solution supposed to contain alcohol, some acetate of soda is

added and sulphuric acid in amount more than sufficient to decompose the acetate. The flask containing the mixture is connected with a Liebig's condenser, placed vertically, and boiled for a few minutes; any volatile vapour is condensed, and falls back again into the flask. On removing the cork, if acetic ether has been produced, it can readily be detected by its odour.

(2.) *Reduction of Chromic Acid or Bichromate of Potash to Oxide of Chromium.*—A crystal of chromic acid, placed in a test-tube, with a fluid containing alcohol warmed to a boiling temperature, is decomposed into the green oxide of chromium. Instead of chromic acid, a test-solution of one part of dichromate of potash dissolved in 300 parts of sulphuric acid may be used. A portion of the liquid to be tried is mixed with twice its volume of concentrated sulphuric acid. On pouring a small quantity of this mixture into a quantity of the test-solution, a deep green is produced where one fluid touches the other. This is a very good test in the absence of other reducing agents, such as formic acid, ether, &c.

(3.) *Dr. Edmund Davy's Test.*—Dr. Davy has proposed a test for alcohol founded on a colour reaction, and produced also by methyl, propyl, butyl, and amyl alcohols, ether and aldehyde. A solution of one part of molybdic acid in ten of strong sulphuric acid, is warmed in a porcelain capsule, and the liquid to be tested allowed to fall gently on it. If alcohol is present, a blue coloration appears either immediately, or in a few moments; the liquid gradually absorbs moisture from the air, and the colour disappears, but it may be reproduced by evaporation.*

(4.) *The production of Iodoform.*—According to Lieben, one part of alcohol in 2000 of water can be detected by adding to some of the warmed liquid a few drops of a 10 per cent. solution of soda, and dropping in a solution of potassium iodide, fully saturated with free iodine, until the liquid is yellowish-brown; then the alkali solution must be added until the whole is colourless, and the mixture allowed to stand for many hours, when a yellowish crystalline deposit of iodoform is obtained. Under the microscope the latter presents the appearance of hexagonal plates, six-rayed, or other varieties of, stellar crystals: $C_2H_6O + 4I_2 + 6NaHO = CHI_3 + NaCHO_2 + 5NaI + 5H_2O$. The objection to this test is, however, that other alcohols, aldehyde, gum, turpentine, sugar, &c., give a similar reaction.†

* *Proceedings of the Royal Irish Academy* [2] ii. 579-582; *Journ. Chem. Soc.*, 7, 1877, p. 108.

† Rajewsky has found that the brain of a rabbit, which had been starved for two days before death, gave a marked reaction for alcohol with the iodoform test, and the same result was obtained from the muscles and

(5.) *The production first of Acetic Acid, then of Kakodyl.*—A very delicate test for alcohol, and one specially suited for its detection in the blood, &c., is recommended by Bucheim.

The finely-divided substances are put in a tubulated retort, and, if acid, carefully neutralised. In the neck of the retort is placed a little porcelain or platinum boat, containing platinum black, and at each end there is a moistened piece of strongly-blued litmus-paper. On warming the retort, if alcohol be present, it is oxidised by the platinum black to aldehyde and acetic acid; hence, the hinder piece of litmus-paper will be reddened, the front one unchanged. If only a drop of acetic acid be present, it is possible to detect it in the following way:—The platinum black is washed, the washing water neutralised with potash, and dried after the addition of a few grains of arsenious acid. On warming the dry residue in a small glass tube, if even a very small admixture of acetic acid be present, the smell of kakodyl will be perceptible.

The Action of Alcohol on Benzoyl Chloride.—This test, proposed by Berthelot, is based on the fact that very small quantities of alcohol decompose benzoyl chloride with the formation of ethyl benzoate. The sample is shaken up in the cold with a few drops of benzoyl chloride; any ethyl benzoate formed sinks to the bottom with the excess of benzoyl chloride. This heavy layer is removed by a pipette, and heated with a little caustic soda or potash, which dissolves at once the benzoyl chloride, but not the ethyl benzoate, and the latter may be recognised by this insolubility, by its general properties, and by its boiling point. It is nearly insoluble in water, burns with a smoky flame, has a characteristic pleasant odour, and boils at 213°.

Mr. J. Hardy has proposed a very simple test for the detection of alcohol, which may be performed as follows:—Two common "Nesslerising" glass cylinders are taken, and a little guaiacum resin, which has been removed from the interior of a freshly broken lump, is shaken up with the sample to be tested. The liquid is filtered, and a few drops of hydrocyanic acid and a drop of very weak solution of sulphate of copper added. Exactly the same process is adopted with an equal bulk of distilled water. On now placing the two liquids in the glass cylinders side by side, over a porcelain plate, the liquid to be tested, if it contains alcohol, will be found of a blue colour decidedly darker than that of the distilled water.

§ 232. *Separation of Alcohol from Animal Matters.*—In order to

tissues of rabbits. He therefore considers that alcohol always exists in the animal organism, or that it is produced during distillation.—*Pflüger's Archiv. für Physiologie*, xi. 122, 127.

obtain alcohol from organic matters (*e.g.*, the contents of the stomach, or the tissues), the following process will be found convenient :—Solid matters, such as the tissues, are cut up as finely as possible, and placed with water in a retort attached to a suitable condenser. Most liquids require no previous preparation, and are merely poured into the retort or flask, as before described; but it is desirable in the treatment of *urine* to add a little tannic acid. About one-third to one-half of the liquid is distilled over into a flask closed by a mercury valve. The product is now made alkaline with caustic potash (which will fix any volatile acid, and expel any volatile alkali), and again distilled, about one-third being drawn over. The liquid is next neutralised with sulphuric acid, to fix volatile alkalies, and redistilled. This final distillate contains all the alcohol, but neither volatile acids nor alkalies. The liquid thus obtained may even now be too dilute to respond conveniently to tests, and it may therefore be digested for some hours with a little caustic lime, and then very slowly distilled. The distillate should finally be carefully measured or weighed, and divided into two parts, one of which serves for the application of the usual tests, the other (if alcohol be found) can be oxidised in the manner described at p. 380, and estimated as acetic acid volumetrically.

J. Bechamp (*Compt. Rend.*, 89, 573, 574) has recently succeeded in obtaining a sufficient quantity of alcohol from the fresh brain of an ox to estimate by specific gravity, and has also separated it from putrefying animal matter. In fact, it is capable of proof, that all putrefaction is accompanied by the production of minute quantities of alcohol, and that the living cells of the body also produce it. Hence, in questions of poisoning, it is not enough to obtain qualitative reactions for alcohol, but the quantity also must be accurately estimated.

ESTIMATION OF ALCOHOL IN SPIRITS AND ALCOHOLIC LIQUIDS.

§ 233. In the examination of alcoholic liquors, one of the analyst's first steps is to determine the percentage of alcohol, and the methods by which this is done are equally applicable (with slight modifications) to all liquids containing alcohol. The percentage is ascertained—

(1.) By distillation, and taking the specific gravity of the distillate.

(2.) By Tabarie's method, applied especially to wines and beers.

(3.) By Geissler's vaporimeter.

(4.) By oxidation into acetic acid, and by several other methods, which are, however, not much in use by the analyst.

(1.) *Distillation.*—A convenient quantity (*e.g.*, 100 cc. of beer or wine, 50 cc. of spirits, measured at 15°·5) is placed in a flask (*a*, fig. 41), having a side tube connected by means of a cork to a

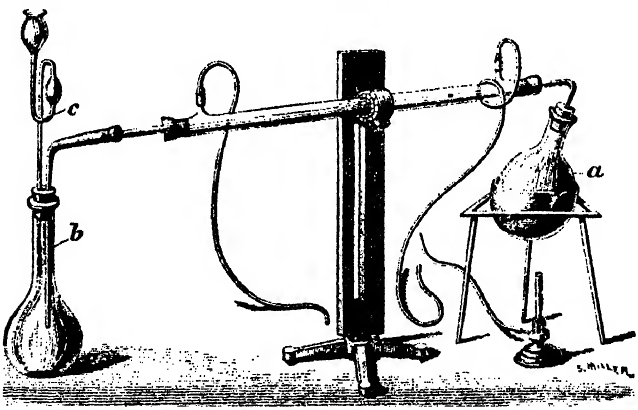

Fig. 41.

Liebig's condenser. The distillate is received in a flask (*b*) provided with a doubly perforated cork, into which the bent tube of the condenser, as well as a tube provided with a mercury valve, to prevent loss, is adjusted; the latter may be readily made by putting a very small quantity of mercury into the bend of an ordinary thistle-head funnel (*c*). This precaution is only necessary when very small quantities are operated upon. Experiments with 50 cc. of spirit distilled into a flask unprovided with a valve, have shown that there is no appreciable loss; but distillation

into an open vessel will always give results far too low. Beer and wine yield the whole of their alcohol when half is drawn over; spirits should be distilled nearly to dryness. In any case, the distillate should be made up to exactly the same bulk as the original liquid at the same temperature, its specific gravity taken in a proper specific gravity bottle, and the percentage of alcohol obtained by reference to the tables given at p. 371. Spirits are best returned as containing so much *proof spirit*, by weight and by volume; wines and beers, so much alcohol per cent., by weight and by volume.

(2.) *Tabarie's method*, when properly performed, is sufficiently accurate for all practical purposes in the case of beers, wines, and similar liquids. The specific gravity is first accurately taken at 15°·5; a measured quantity—say 100 cc.—is then boiled long enough to evaporate away the whole of the alcohol, made up to the original bulk *at the same* temperature, and its specific gravity again determined. From these data the specific gravity of the liquid, which, if it had been condensed, would have collected in the flask before-mentioned, is determined. Thus, specific gravity of the liquid before boiling, divided by the specific gravity of the de-alcoholised liquid = specific gravity of the diluted alcohol which has been boiled away. An actual example will suffice:—A beer, before boiling, had a specific gravity of 1·014; after boiling, and on making it up to the original bulk, its specific gravity was 1·0172; now $\frac{1\cdot014}{1\cdot0172}$ = ·9968, and on reference to the table at p. 371, ·9968 is found to correspond to 1·7 per cent. of alcohol.

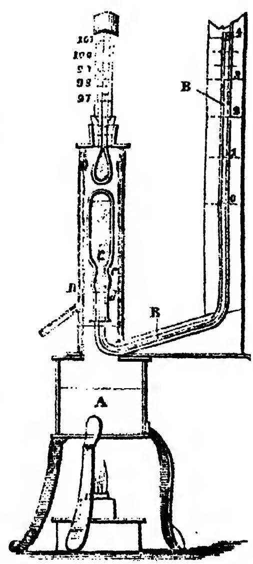

Fig. 42.

(3.) *Geissler's Vaporimeter* is capable of giving sufficiently accurate results for technical purposes, and as it has the advantage of great expedition, it may always be used to supplement and check other methods which take more time. It depends on the measurement of the tension or elastic force of the vapour of the liquid, as indicated by the height to which it raises a column of mercury. The apparatus (see fig. 42) consists of four parts—viz., (1.) A brass vessel A, containing water; (2.) a doubly bent tube, BB, fastened to a scale; (3.) a cylindrical vessel C, which is filled with mercury and the fluid to be tested; (4.) a brass vessel D, in the upper part of which there is a

thermometer. By removing the bent tube and its connections from A, it may be turned upside down, and C detached; the alcoholic fluid is then poured in so as to fill the space between *c* and *d*, which, when the instrument is inverted, is empty. It is now connected with the bent tube, and adjusted exactly as in the figure, the water made to boil in A, when the mercury runs up to a certain height in the tube, and the percentage is directly read from the scale. Should the thermometer not register 100°, certain corrections must be made, which is most conveniently done by a table, sold with the instrument. Care in this manipulation must always be taken to exclude air from the bulb. The author has found it always necessary to test various points of the scale with known mixtures of alcohol and water, and to draw up a table of corrections. With this precaution, it will be found a most useful instrument.

(4.) *Oxidation into Acetic Acid* is an extremely accurate method of determining vinic alcohol, and is specially applicable to small quantities. Dr. Dupré recommends the following process*:— A small quantity of the distillate, representing about a gramme of alcohol, is put in a small strong assay-flask, and mixed with 10 cc. of an oxidising solution, composed of 147 grms. of bichromate of potash and 220 grms. of sulphuric acid, made up to 1,400 cc. by water. The flask is well stoppered by caoutchouc, and firmly tied down by canvas and string. It is then suspended upright in a water-bath (the neck being above the water), and heated for two hours between 80° and 90°. The flask is next removed, and the excess of bichromate reduced by zinc and sulphuric acid; the solution is transferred to a small retort (adding some sulphuric acid and bits of tobacco-pipe), and distilled over from a spermaceti-bath (see fig. 41). It will be found necessary to distil at least thrice nearly to dryness, each time adding water to the contents. The united distillates contain acetic acid, the result of the oxidation of the alcohol. This acetic acid may be determined by a volumetric solution of soda, and the amount of alcohol to which it is equivalent calculated by the following short table:—

Acetic Acid.		Alcohol.
1	=	·7666
2	=	1·5332
3	=	2·2998

* It has been shown by Wanklyn that alcohol may also be oxidised into acetic acid very readily by an alkaline solution of permanganate of potash; it would appear that in this case there is no previous formation of aldehyde. A. Letteltür also finds that an ammoniacal solution of copper-oxide at 180° has the same effect. *Compt. Rend.*, 89, 1105.

Acetic Acid.		Alcohol.
4	=	3·0664
5	=	3·8330
6	=	4·5996
7	=	5·3662
8	=	6·1328
9	=	6·8994
10	=	7·6666

There are several other methods of estimating alcohol, but the above are the most practical and efficient; and whenever the amount of alcohol is important (as, for example, in the case of spirits) the analyst should determine it in at least two different ways. The specific-gravity methods presuppose the presence of ethylic alcohol only; but it is sometimes necessary to test fluids also for methylic and amylic alcohols. For these the following processes are available:—

§ 234. *Methylic Alcohol.*—100 cc. of the suspected spirit are distilled twice, having been rendered alkaline during the first process and acid during the second, about two-thirds being distilled over each time. The distillate is now shaken up with dry potassium carbonate, and, after standing over night, the upper layer is taken off by a syphon or pipette, and again twice distilled, about 15 cc. being driven over. This will contain any methylic alcohol present in the original 100 cc. A portion of the distillate is now diluted with water to a strength from 10 to 15 per cent., and in this diluted spirit the alcohol determined—(1.) By specific gravity; (2.) by Geissler's vaporimeter; and, (3.) by oxidation into acetic acid. If ethylic alcohol alone is present, all three methods fairly agree. The specific gravity will give the total amount of both alcohols, the specific gravity of aqueous methylic and ethylic alcohols being almost identical; but since methylic alcohol has a higher vapour tension than ethylic, Geissler's vaporimeter will give a higher result. The oxidation process will, on the other hand, give a lower result, for methylic alcohol yields water and CO_2, so that the acetic acid found is derived wholly from the ethylic alcohol, and the difference between the strength thus found and that derived from the specific gravity gives a rough indication of the proportion of methylic alcohol present. If the methylic alcohol is in sufficient quantity, instead of the usual slight vacuum on opening the flask, there is an escape of carbonic anhydride, and there is no reason why this gas should not be either absorbed or collected and estimated.

Dr. Dupré gives the following example. A pure whisky showed—

Strength by specific gravity,	9·83 per cent.
„ Vaporimeter,	9·75 „
„ Oxidation,	9·75 „

The same whisky, adulterated with 10 per cent. of ordinary methylated spirit, and tested, gave—

Strength by specific gravity,	. .	10·08 per cent.
,, Vaporimeter,	. . .	10·45 ,,
,, Oxidation,	. . .	9·50* ,,

The remainder of the distillate may be used in producing methyl-aniline violet or oxalate of methyl.

The general process for the production of methyl-aniline violet is as follows:—10 cc. of alcohol, with 15 grms. of iodine and 2 grms. of red phosphorus, are put into a small flask, and distilled into 30 or 40 cc. of water. The alcoholic iodide which settles to the bottom is separated by a pipette, and collected in a flask containing 5 cc. of aniline. If the action be too violent, the flask can be cooled with cold water; if too slow, a little heating may be necessary. At the end of an hour the crystals are dissolved in hot water and boiled, an alkaline solution is afterwards added, and the bases rise to the top in the form of an oily stratum, which may be separated by bringing the oil, by the addition of water, on a level with the neck of the flask. The oxidation of the bases may be effected in various ways, but best by pouring a cubic centimetre of the oily liquid on 10 grms. of a mixture formed of 100 grms. of quartz sand, 2 of chloride of sodium, and 3 of nitrate of copper. After incorporation it is introduced into a glass tube, and kept at 90° in a water-bath for eight or ten hours; it is ultimately exhausted by warm alcohol, thrown on a filter, and made up to 100°. If the alcohol was pure the tint is red; if it contained 1 per cent. of methyl alcohol the colour, by the side of the preceding, is manifestly violet; with 2·5 per cent. the shade is a very distinct violet; and with 5 per cent. it is considerably darker. The process may be made quantitative by having volumetric solutions of methyl and ordinary alcohol. Very minute quantities of methyl alcohol may be detected by adding 5 cc. of the liquid to 95 cc. of water, and then again diluting 5 cc. of this liquid with 400 cc. of water, and heating it in a porcelain capsule. Fragments of white merino (free from sulphur), immersed in the liquid for half an hour, will remain white, if the alcohol was pure; if methyl was present, they will be of a violet tint.†

Oxalate of Methyl may be obtained by mixing the distillate with half its bulk of sulphuric acid and double the quantity of hydropotassic oxalate. The whole should stand in the retort for

* Note on the Examination of Whisky and other Spirits for Methylated Spirit and Fousel Oil, by Dr. Dupré. *Analyst*, i., 1876, p. 4.

† A. Riche and Brady, *Comptes Rendus*, vol. xxx., p. 1096.

twenty-four hours, and then be distilled. Crystals appear after a time in the cooler parts of the flask or retort; their composition is $(CH_3)_2C_2O_4$. It would also be quite possible to produce such compounds as the salicylate of methyl, &c.

Formic Acid.—It has been already stated that methyl alcohol, when fully oxidised, is resolved into CO_2 and water. This takes place in two stages; first, formic acid is produced, and then this formic acid breaks up. Thus:—

(1.) Methyl Alcohol, $CH_4O + O_2$	=	Formic Acid, $CH_2O_2 + H_2O$
(2.) Formic Acid, $2CH_2O_2 + O_2$	=	$2CO_2 + 2H_2O$

It hence follows that if a spirit be distilled in the manner recommended by Dr. Dupré, and only partially oxidised, it is possible to get formic acid, which has some very characteristic properties. To obtain this result a small portion of the distillate, 2 to 4 cc., is taken, and 3 grms. of potassic dichromate are added, with an equal quantity of pure sulphuric acid, and four or five times as much water. This is allowed to act for twenty minutes, and then distilled; the liquid is alkalised with sodium carbonate, evaporated to half its bulk, acidulated with acetic acid, transferred to a test-tube, and then heated gently with a 5 per cent. solution of nitrate of silver. If formic acid has been produced, there is a distinct precipitate of metallic silver.

§ 235. *Fousel Oil* is the name given by most chemists to amylic alcohol; it may, however, be conveniently applied to the mixture of the higher homologues of ethylic alcohol. Dr. Dupré* detects fousel oil by oxidising one or two grms. of alcohol, previously distilled (if necessary) in the manner already described. When cool the flask is opened, the excess of dichromate reduced by zinc, and the acids produced distilled off. The acid distillate is neutralised with a standard solution of normal soda, the solution evaporated to a small bulk, and transferred to a retort. An amount of normal sulphuric acid, equal to one-twentieth of the normal alkali used, is now added, and the contents of the retort are distilled to dryness in an oil-bath, the temperature being allowed to rise to about 130°. Water is then added, with a further quantity, one-twentieth, of normal acid, and the contents re-distilled to dryness. Some water is now poured on the dry residue in the retort, and it is again distilled, the latter operation being repeated three times. The distillates from these various operations are united, neutralised by carbonate of barium, the solution boiled, filtered, and evaporated to dryness, the

* *Op. cit.*

residue dried at 130°, and weighed. The barium salt is converted into sulphate in the usual manner, and the percentage of barium determined. The data are now at hand to determine the presence of fousel oil in the sample, and the approximate quantity. The barium salt of the acid produced by the oxidation of fousel oil (Barium valerianate, $Ba(C_5H_9O_2)_2$,) contains 40·41 per cent. of barium. The barium salt of the acid derived from the oxidation of pure alcohol (Barium acetate, $Ba(C_2H_3O_2)_2$,) contains 53·72 per cent. of barium. If the alcohol is free from fousel oil, the barium found will closely approximate the percentage mentioned; but if the higher alcohols are present, the percentage will be lower, and a fair approximation to the amount of fousel oil will be arrived at by estimating the salt as a mixture of baric acetate and valerianate, and calculating out the percentages on the usual principles.

BRANDY.

§ 236. Brandy, in its present form (Cognac), is a spirit derived from the distillation of wine; inferior varieties are made from the refuse of grapes, with admixture of other materials.* The constituents of brandy are—alcohol, water, acetic, œnanthic (ethyl pelargonate), butyric, and valerianic ethers, small quantities of grape sugar, minute quantities of a volatile oil, colouring-matter, a trace of tannin, acetic acid, and a little fixed acid. The specific gravity of genuine brandies varies from ·929 to ·934; the solids from 1 to 1·5; ash, ·04 to ·2; acidity, ·01 to ·05 (reckoned as tartaric acid); and the sugar from 0 to ·4 per cent.

The adulterants to be looked for are—methyl and amylic alcohols, tannin in excess, sulphuric acid, lead, copper, zinc, and hot principles, such as cayenne. The estimation of alcohol and the examination of the distillate are elsewhere described (see p. 378 *et seq.*) Any acetic acid will be found in the distillate, and can be estimated by volumetric solution of soda. Fixed free acids

* The brandy made in England is for the most part artificial. A very usual process is to add to every 100 parts of proof spirit from half-a-pound to a pound of argol, some bruised French plums, and a quart of good Cognac; the mixture is then distilled, and a little acetic ether, tannin, and burnt sugar added afterwards.

Artificial Cognac is sometimes made by oxidising palm-oil by potassic dichromate and sulphuric acid, and then distilling it with 70 per cent. of alcohol and concentrated sulphuric acid. Œnanthic ether is among the products.

will remain in the residue, and (if no free mineral acid is detected) may be estimated volumetrically, and returned as tartaric acid (1 cc. of d.n. soda = ·0075 tartaric acid).

If the residue taste hot and pungent, some sophistication, such as capsicum, must be present; an attempt should be made to separate such hot substances in a comparative state of purity by benzole, ether, &c.

If the brandy is coloured by caramel alone, on the addition of a persalt of iron there will be no deepening of tint; if, on the contrary, the colouring be derived from the cask, and the brandy contain tannin, it will deepen very decidedly in colour.

Since it appears that in some of the recipes of the trade tincture of oak bark is used,* should the precipitate by a persalt of iron be very evident, the amount of tannin must be estimated. The direct addition of hydric sulphide to acidified spirits produces a colour sufficiently dark to be noticed should lead or copper be present, especially if an equal bulk of the unsulphuretted spirit be compared side by side. If zinc be sought, it will be best to add carbonate of soda, evaporate to dryness, and proceed as in the article on "Zinc" in the second part of this work, to which portion also the reader is referred for special processes for the detection of lead and copper.

RUM.

§ 237. The best rum is distilled from fermented molasses, inferior kinds from the *débris* of the sugar-cane. In France a considerable amount of spirit is also derived from the molasses of the beetroot-sugar factories. The specific gravity of rum varies from ·874 to ·926; it is usually a strong spirit, genuine rum never falling below 50 per cent. of alcohol, and often reaching as high as 70 per cent. It is always slightly acid (about ·5 per cent.) The solid residue varies from ·7 to 1·5 per cent. It may contain sugar; the proportion of ash is very small, seldom more than ·1 per cent. The analysis is carried out strictly on the principles before described.

* Mr. Griffin found a large quantity of tannin in a sample of brandy. He explains the circumstance by the following receipt for the manufacture of Cognac:—Take of acetic ether three quarters of a pound, French wine eight quarts, oak-bark tincture (made with a quarter pound of oak bark and half a quart of spirit) half a quart, purified spirits so much as to bring the whole to 150 quarts of 54 per cent. by Tralles.—"Chemical Testing of Wines and Spirits." By John J. Griffin, F.C.S., London, 1872.

WHISKY.

§ 238. *Whisky* is one of the corn spirits, and is usually manufactured from malted grain. The Scotch distillers, for the most part, make it entirely from a malt mash, the Irish use malt and raw grain; but in both countries there are considerable differences in its manufacture. The new whisky, impregnated with fousel oil, is called "pot-still whisky." This liquor is often blended with so-called improvers—"Hambro" sherry, prime wine, &c. The specific gravities of whiskies is usually from ·915 to ·920; alcoholic strength from 50 to 60 per cent.; total extract under 1 per cent.; it has a minute quantity of volatile acid (seldom, perhaps never, so high as ·1 per cent.), reckoned as acetic, and a trace of ash. If sugar is found it must have been added.

The chief adulterant popularly supposed to be mixed with whisky is potato spirit, or fousel oil; but besides this, methyl alcohol, creosote, fixed acids, and, generally speaking, the sophistications used for the other spirits, have either been proved, or their presence suspected, as fraudulent additions. With regard to fousel oil, small quantities in ordinary whisky are incidental to its manufacture, and not an adulteration. The only estimations of the exact quantity of fousel oil in whisky that we have, are probably those contained in Dr. Dupré's paper before quoted.* Dr. Dupré found in a sample of Scotch whisky—

For 100 of Ethylic Alcohol, . .	0·19	per cent.	Amylic.
Cape Smoke, ...	0.24	,,	,,
Common Samshoe.	0·18	,,	,,
Fine ,, ...	0·13	,,	,,

Since these appear to be the only determinations worthy of any credit, it is difficult to say what quantity of amylic alcohol denotes adulteration, and the question becomes a medical one—viz., whether fousel oil is injurious or not; if it is, how much is injurious?

§ 239. That fousel oil *is* injurious (we may say, indeed, poisonous) is evident enough from experiments on animals and men—*e.g.*, Eulenberg † allowed 30 grms. of amyl alcohol to evaporate in hot sand in a zinc box in which a kitten was confined. After half the quantity had been put in, the symptoms immediately commenced, and in an hour the animal lay partly insensible, breathing with difficulty, and shivering. There was, however, no full narcosis, and it recovered in four days. In another experiment, in which 40 drops of amyl alcohol had been

* *Analyst*, i., 1876, p. 6.
† *Gewerbe Hygiène*, 1876, p. 440.

administered to a kitten, after seventeen minutes there were palpitation of the heart, irregular breathing, and relaxation of the limbs, and in twenty-two minutes there was full anæsthesia. The animal recovered after a short time, the heart's action remaining more frequent than usual until the next day. Cross * observed similar symptoms in pigeons and kittens; in the latter the respiration was stertorous. Rabuteau † states that 1 of amyl alcohol in 500 of water causes anæsthesia in frogs in twenty minutes; the heart's action becomes slower, and the skin dark, and in about two hours death occurs, the cardiac pulsations gradually ceasing. Dr. Furst of Berlin killed a rabbit with about 7·6 grms. (2 drachms), injected into the stomach; another, however, recovered from the same dose.

Action on Man.—Men engaged in the manufacture of potato-spirit suffer from headache and general nervous indisposition, unless the vapours are conducted away from them. An experiment by Cross on himself showed that the vapour caused intense aching and heaviness of the head, and other unpleasant symptoms. It has also been shown that 20 cgms. (3·0 grains) of amyl alcohol taken internally produce slight symptoms, the action being first stimulating, then depressing.

From the foregoing we are now in some degree able to judge what amount of amylic alcohol would probably have immediate injurious effects; as to the chronic effects of small doses nothing definite is known. Turning to Dr. Dupré's first sample (a Scotch whisky containing ·19 of amylic to every 100 of ethylic alcohol, the whisky itself containing 54·5 per cent. of alcohol), it would appear that such a whisky has about ·49 of amylic alcohol to the ounce. A person taking 2 ounces of such a liquid would thus swallow nearly a grain of amylic alcohol, and if it contained three times the quantity, the active properties of the amylic would be added to that of the ethylic; for it would then be equal to about 3 grains, the lowest amount at which distinct effects can be obtained. Anything, therefore, like a grain and a half of amylic alcohol per ounce (irrespective of the question whether such a whisky may be pronounced *adulterated* or not), may certainly be considered injurious to health. The analysis of whisky is carried out precisely upon the principles already detailed.

§ 240. The prosecutions for mere dilution of whisky ‡ have

* Cross: De l'Alcohol Amylique et Methyl sur l'Organisme. Thèse. Strasburg, 1863.

† Rabuteau: Ueber die Wirkung des Æthyl, Butyl, und Amyl Alkohols. *L'Union*, Nos. 90, 91, 1870; *Schmidt's Jahrb.*, Bd. 149, p. 263.

‡ The legal limit of dilution of brandy, whisky, or rum is 35 degrees under proof. (See p. 48.)

been rather frequent, especially in the north of England; but very few *convictions* for other adulterations appear to have been obtained. The following case presents sufficient points of interest to deserve quotation :—

At the Greenock Police Court, W. D. was accused of selling to two women four gills of whisky adulterated with fixed acid in a free state. . . . The analyst stated that the liquor contained—

By weight per cent.		
34·5	Alcohol	= 72·4 proof spirit.
6·42	Fixed acid.	
9·87	Volatile acid.	
32·20	Ash.	

The adulteration did not materially increase the weight of the whisky, and it was not hurtful, but the liquor was of inferior quality. Although volatile acid was sometimes found in whisky from natural causes, it did not occur in so large a quantity. He was of opinion that it had been added in the present case in the form of sherry wine. Volatile acid had the quality of changing the tone, and giving it a little flavour. The fixed acid could not be present in pure whisky unless it had been added. A penalty was imposed by the court.—*San. Record*, i., 1874, 442.

GIN.

§ 241. Gin is a spirit flavoured with various substances. The different receipts used in the trade include—

- Juniper berries.
- Coriander seeds.
- Orris root.
- Angelica root.
- Calamus root.
- Cardamom seeds.
- Liquorice powder.
- Grains of Paradise.
- Cassia buds.

These generally impart their essential oils to the spirit. A few of the more important only will be described here.

§ 242. *Oil of Calamus.*—The oil distilled from the root of the calamus is a somewhat thick, yellow, or brownish-yellow oil; neutral, specific gravity 0·950 to 0·952; after rectification, 0·950; boiling point, 196°. It contains oxygen, is but slowly changed by sodium, and does not fulminate with iodine. It dissolves in all proportions in alcohol and bisulphide of carbon. The spirituous solution of the oil takes a brown colour on the addition of a little chloride of iron.

§ 243. *Oil of Cardamoms* is a pale yellow oil, with a strong smell of cardamoms, of neutral reaction, of specific gravity 0·92 to 0·94. It contains a stearoptene of the formula $C_{10}H_{16}3H_2O$.*

* HUSEMANN.—"Die Pflanzenstoffe."
DUMAS and PÉLIGOT: *Ann. Chim. Phys.* [2], lvii. 334.

§ 244. *Angelica root* contains a volatile acid—*Angelic acid*—a bitter principle, a crystalline substance—*Angelicine*—a resinous substance, an essential oil, and other constituents.

Angelic Acid, $C_5H_8O_2$, forms transparent glittering prisms and needles, melting at 44° to 45° into an oil, which may be solidified at 0° into a crystalline solid. If the heat be raised up to 190° it boils and distils unchanged; it is inflammable, burning with a luminous flame. The acid reddens litmus, and has the odour of the root. It scarcely dissolves in cold water, but is soluble in hot, in alcohol, ether, turpentine, and the fatty oils. It forms salts with bases, which lose a part of the acid on evaporation. It precipitates lead and silver salts white; iron salts, dark yellow; and copper, bluish. By the aid of hydric iodide and red phosphorus, acting at 180° to 200°, angelica acid is changed into valerianic. Melting the acid with KHO decomposes it into propionate and acetate of potash.

Angelicine is, according to Brunner, probably identical with *hydrocarotin*, a principle described by Husemann, found in the *Daucus carota*, L., and to which the following formula is ascribed, $C_{18}H_{30}O$. Hydrocarotin, or angelicine, forms colourless, large, thin plates, without smell or taste, swimming in water, and becoming at 100° hard and brittle. At higher temperatures (120°·5) it melts without loss of weight to a yellow fluid, which solidifies as a resinous mass, and cannot be again crystallised. It is readily soluble in ether, chloroform, carbon bisulphide, benzine, oil of turpentine, and warm olive oil. It is not changed in colour by concentrated hydrochloric acid; fuming nitric acid dissolves it with the evolution of gas. Concentrated sulphuric acid dissolves it to a red fluid, depositing brownish-white flakes on dilution with water.

Angelica Oil is colourless, and lighter than water; it has a penetrating odour and camphor-like taste, and resinifies on exposure to the air.*

§ 245. *Oil of Coriander* is a pale yellow oil, smelling like the fruit; of specific gravity ·871 at 14°, and a portion distilling over at 150°. The volatile part corresponds to the formula

* *Bibliography.*
Alscher.—*Ber. d. deutsch. Chem. Ges.*, 1869, 685.
Brunner, Carl.—*N. Rep. Pharm.*, xxiv. 641–665.
Buchner, A.—*Repert. Pharm.*, lxxvj.
Chiozza.—*Ann. Chim. Phys.* [3], xxxix. 435.
Husemann.—"Die Pflanzenstoffe." Berlin, 1871.
Jaffe.—*Ann. Chem. Pharm.*, cxxxv. 291.
Mayer and Zenner.—*Ann. Chem. Pharm.*, lv. 317.
Reinsch.—*Jahrb. Pharm.*, vii. 79.

$C_{16}H_{16}H_2O$; the portion of a higher boiling point to $4C_{10}H_{16}H_2O$. If both portions are distilled with phosphoric anhydride, a powerfully odorous camphor, $C_{10}H_{16}$, is produced.*

§ 246. *Oil of Juniper* is contained in the unripe berries of the common juniper, in the proportion of from ·4 to ·75 per cent. It is colourless, or of a pale yellow, dissolving with turbidity in twelve parts of alcohol of 83 per cent. Miscible in all proportions with ether and bisulphide of carbon. Smell and taste mildly aromatic. Specific gravity 0·862 to 0·874, but the poorer commercial samples often have a specific gravity of 0·860. The perfectly colourless oil does not fulminate with iodine, but the commoner kinds explode powerfully.† If from 5 to 6 drops of the oil be placed in a test-tube, and five times its bulk of sulphuric acid be added, much heat is developed with the evolution of vapour, and the fluid becomes dark yellow-red and turbid; on now diluting with 10 cc. of 90 per cent. alcohol, the colour changes to a somewhat dirty rose tint. The pure oil boils between 140° and 150°; it polarises to the left. On exposure to the air, oxygen is absorbed; and on long standing, colourless tables of juniper camphor are separated. This camphor melts and sublimes without decomposition, is easily soluble in ether and alcohol, and may be obtained in feathery crystals.

The action of warm water on juniper oil, if kept up for some considerable time, results in the formation of a crystalline hydrate. Oil of juniper is officinal in all the Continental pharmacopœias, as well as our own. In such large doses as from 15 to 30 grms., it is fatal to kittens, apparently acting in the same way as turpentine.‡

§ 247. *Analysis of Gin.*—The analyst should find in good gin at least 80 per cent. of proof spirit, and a variable amount of sugar and flavouring matters, seldom much over 5 or 6 per cent. Sulphuric acid, sulphate of zinc, alum, and lead should always be looked for. Many writers seem to imagine that grains of paradise is an *adulterant*. It is, however, in its properties merely a

* HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
KAWALIER.—*Journ. Pract. Chem.*, lviii. 226.

† It is said that the oil from the unripe fruit explodes, that from the fully ripe berries losing this property.

‡ *Bibliography.*

HIRSCH.—"Prüfung der Arzneimittel." Berlin, 1875.
HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
SIMON.—"De Olei Juniperi Berol.," 1841. *Berlin Med. Ver. Ztg.* 19, 1844.
STEER.—*Chem. Centralbl.*, 1856–60.
SOUBEIRAN et CAPITAINE.—*Journ. Pharm.* [2], xxvj. 78.
ZAUBZER.—*Repert. Pharm.*, xxii. 415.

pepper, and much nonsense has been talked about it. It is very doubtful whether any just conviction would be obtained for the addition of any harmless flavouring to the spirit; nearly all prosecutions hitherto have been for dilution, and for dilution only. It appears that no genuine gin * is sold to the retailer 22 under proof, but the standard fixed by the 6th section of the Amended Act (see p. 48) lays down the limit of 35 degrees under proof, and anything below this must be returned by the analyst as adulterated.

The alcohol should be determined by distillation, as before described (p. 378), and the percentage in the distillate estimated by specific gravity, and, if necessary, in other ways. Neither methyl-alcohol nor fousel-oil appears to have been found in gin.

The residue after the distillation may be treated with petroleum ether, benzine, &c., as in Dragendorff's process for the testing of beers. The essential oils will be taken up by the petroleum ether, and may be identified by their odour and taste, and (if enough is obtained) by their physical properties. Sulphuric acid, if in a free state, may be separated by quinine, as recommended under the article "Vinegar." The detection of alum, lead, and zinc is elsewhere described.

ARRACK.

§ 248. The best qualities of arrack are manufactured by distillation of the fermented juice of the cocoa-nut tree, palmyra tree, and other palms; the coarser kinds are made from the distillation of fermented rice liquor. Arrack is nearly colourless, a slight tinge of yellow or brown being only observed in samples kept in casks for a length of time. The average strength and composition of arrack are as follows:—

* In an appeal case (heard before the legal limit was fixed) before Baron Cleasby and Mr. Justice Grove (*Fashler* v. *Stevenilt*), the analyst proved that the gin was 44 degrees below proof. The judges affirmed the conviction. Baron Cleasby thought the conviction was right. When the respondent asked for gin he meant such gin as is ordinarily sold; and to sell him such gin as that in question was to sell, to the prejudice of the purchaser, gin which was not of the quality demanded. The amount of water proved to have been discovered with the gin afforded evidence that it had been added for the purpose of fraudulently increasing its measure. Mr. Justice Grove concurred; in his opinion, when it was proved that the gin contained so much more water than gin as ordinarily sold, the onus was thrown on the seller of proving that he was not aware of the state in which it was.

		Per cent.
Specific gravity,	·9158	
Alcohol,		52·700
Extract,		·082
Ash,		·024
Water,		47·194

The Hindoos and Malays consume large quantities of arrack. It would appear in the East to be occasionally drugged, and Indian hemp and the juice from solanaceous plants are said to be employed for this purpose.

LIQUEURS OR CORDIALS.

§ 249. The term cordial, liqueur, &c., is applied to a number of liquids which essentially consist of very strong spirit, flavoured with essences, and often very brightly coloured by vegetable colouring-agents, such as turmeric, cochineal, &c. Occasionally injurious colours are used, and salts of copper, picric acid, and impure aniline dyes have been detected. Of the liqueurs, absinthe is the most important in relation to health, and will be considered separately. The alcoholic strength and general composition of a few others are as follows:—

	Specific gravity.	Alcohol by weight.	Extract.	Cane Sugar.	Other Extractive Matters.	Ash.
Bonekamp of Maagbitter,	·9426	42·5	2·05	...	...	0·106
Benedictine-bitter,	1·0709	44·4	36·00	32·57	3·43	0·043
Ingwer,	1·0481	40·2	27·79	25·92	1·87	0·141
Crême-de menthe,	1·0447	40·7	28·28	27·63	0·65	0·068
Anisette de Bordeaux,	1·0847	35·2	34·82	34·44	0·38	0·040
Curaçoa,	1·0300	47·3	28·60	28·50	0·10	0·040
Mümmel-liqueur,	1·0830	28·0	32·02	31·18	0·84	0·058
Pfeffer-munz liqueur,	1·1429	28·6	48·25	47·35	0·90	0·068
Swedish Punch,	1·1030	21·6	36·61	...	...	...

ABSINTHE.

§ 250. Absinthe is a yellowish-green liqueur, which contains, as a peculiar and distinctive ingredient, a poisonous oil having a deleterious action on the nervous system. This, "*worm-*

wood oil," is the produce of the "*Artemisia absinthium.*" Other flavouring oils are always present, such as peppermint, angelica, cloves, cinnamon, and aniseed. The green colour is produced by the juice of spinach, nettles, or parsley, or, in other words, it is due to chlorophyll. The absorption-spectrum of properly made absinthe, is the same as that of chlorophyll. Most samples of absinthe contain sugar. The average composition of the liqueur as consumed in London (where its use is on the increase) is as follows:—

	Per cent.
Absolute alcohol,	50·00
Oil of wormwood,	·33
Other essential oils,	2·52
Sugar,	1·50
Chlorophyll,	traces
Water,	45·65

On diluting absinthe the essential oils are thrown out of solution, and the liquid becomes turbid. The reaction is always slightly acid, due to a trace of acetic acid.

Adulterations of Absinthe.—The composition of absinthe appears to be fixed by no definite standard of strength; therefore, practically, the analyst has to look only for such substances as injurious colouring-matters and metallic impurities. Sulphate of indigo with turmeric is not unfrequently employed as a colouring agent, and similarly picric acid has been detected, and salts of copper. The latter is readily discovered by diluting the liqueur and adding ferrocyanide of potash, which, if copper be present, will give a brown coloration; picric acid and indigo are detected in the way elsewhere described. (See *Index.*)

Analysis of Absinthe.—The alcohol may be determined by distillation, after diluting the liqueur to cause the oils to separate, and getting rid of some portion by filtration. To make an estimation of the essential oils, a measured quantity of the liqueur is diluted to twice its volume by the addition of water; carbon disulphide is added, and the mixture shaken up in the tube described at p. 69. The carbon disulphide dissolves all the essential oils, and on evaporation leaves them in a state pure enough to admit of their being weighed. Absinthe, when taken habitually and for a lengthened time, produces a peculiar train of nervous symptoms which the French physicians affect to distinguish from the similar symptoms produced in inebriates by alcohol. In epilepsy caused by indulgence in absinthe, M. Voisin states, as the results of clinical observation, that the number of fits is far greater than in alcoholic epilepsy.

FERMENTATION: FERMENTED LIQUORS.

> "The chemical act of fermentation is essentially a correlative phenomenon of a vital act beginning and ending with it. I think that there is never any alcoholic fermentation without there being, at the same time, organisation, development, and multiplication of globules, or the continued consecutive life of globules already formed."—*Pasteur.*

§ 251. Fermented liquors are those manufactured by fermentation—*i.e.*, a peculiar, low vegetable growth has been allowed to grow and multiply, assimilating material in one form, and excreting it in another, and this process has evolved, with other by-products, carbon dioxide and alcohol. Fermentation used to be considered as a sort of special action; but modern research recognises a great variety of ferments, and it is a question whether all animal and vegetable cells, in the exercise of their normal functions, do not act in a similar manner to the environing fluids, as do the organisms more distinctively called "ferments."

In normal alcoholic or spirituous fermentation, as in the manufacture of beer, a minute unicellular plant, "yeast," grows and multiplies, and splits up the sugar, as in the following equation:—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2,$$

that is, one molecule of sugar furnishes two of alcohol and two of carbon dioxide. In ordinary practice this complete reaction never occurs, but if by the constant removal of carbon dioxide and alcohol, by means of a mercury pump, atmospheric air be excluded, the equation is nearly realised. M. Pasteur, in his quantitative research on the products of ordinary fermentation,* found that 100 parts of cane-sugar, corresponding to 105·26 parts of grape-sugar, gave nearly

Alcohol, . . .	51·11	
Carbon dioxide,	48·89	according to Gay Lussac's equation.
	0·53	excess over " "
Succinic acid, . .	0·67	
Glycerine, . .	3·16	
Matter united with ferments, . .	1·00	
	105·36	

* The method adopted by M. Pasteur to detect and measure quantitatively the glycerine and succinic acid contained in a fermented liquid, was as follows:—"The liquid, when the fermentation was over, and all the

M. Monoyer * has represented Pasteur's results in the form of the following equation :—

$$4(C_{12}H_{24}O_{12}) + 6H_2O = 2(C_4H_6O_4) + 12(C_3H_8O_3) + 4CO_2 + O_2,$$

the free oxygen being supposed to serve for the respiration of the yeast cells. Pasteur's equation is far more complex, and represents no free oxygen as produced; yet the fact of fermentation going on briskly in a vacuum, as well as other considerations, points to the probable correctness of Monoyer's supposition.

As a secondary product, there is also constantly acetic acid. This is generally considered to originate from the ferment itself. With ethyl-alcohol there is also produced, when complex matters are fermented, several other homologous alcohols. For example, if potatoes are fermented, on distilling off the more volatile portions, and collecting separately the final distillate, this is found to consist of propyl, butyl, amyl, caproic, œnanthyl, and caprylic alcohols.†

§ 252. *Yeast.*—There are no less than three methods of causing the wort of beer to ferment, but none of the three presents any very distinct variety of the yeast ferment. The one generally employed in England is what is called surface fermentation, in which the starch of the malt is changed into sugar by successive infusions, and the fermentation takes place at from 15° to 18°. This in breweries is done in large open vats; the yeast floats on the surface, and can be removed by skimming.

The second method, more in use in Germany, is fermentation

sugar had disappeared (which required from fifteen to twenty days under good conditions), was passed through a filter, accurately weighed against another made of the same paper. After having been dried at 100°, the dried deposit of the ferment collected at the bottom of the vessel was also weighed. The filtered liquid was subjected to a very slow evaporation (at the rate of from twelve to twenty hours for each half litre); when reduced to 10 or 20 cc. the evaporation was completed in a dry vacuum. The syrup obtained was next exhausted with a mixture of alcohol and ether (1 part alcohol of 30° and 1·5 parts ether), which extracted completely all the succinic acid and glycerine. The ether-alcohol was distilled in a retort, then evaporated in a water-bath, and afterwards in a dry vacuum. To this was added a little lime water, to fix the succinic acid, and again the mixtur was evaporated, and then the glycerine was separated from the succinate of lime by ether-alcohol, which only dissolved out the glycerine. This ether-alcohol solution on evaporation, which was finished as before in a dry vacuum, left the glycerine in a state fit to be weighed, and the calcium succinate was purified by treatment with alcohol of 80 per cent., which only dissolved out the foreign matters."—*Schützenberger on "Fermentation."* Lond., 1876.

* "Thèse de la Faculté de Médicine de Strasbourg."

† M. Jeanjean has separated camphyl-alcohol ($C_{10}H_{16}O$) from the distillate of madder.

by sedimentary yeast (*Unterhefe*). The starch is transformed by decoction, and the temperature (12° to 14°) is much lower than the former. The yeast forms a sediment on the bottom; and when the first and most active fermentation is over, the clear liquid is run off into proper vessels; but the yeast not having been all deposited, a slow fermentation still goes on for a long time.

A third method, employed in Belgium, is to leave the wort to itself, having first placed it under proper conditions.

The microscopical appearance of yeast is that of a number of round or oval cells, from ·00031 to ·00035 in. (·008 to ·009 mm.) in their greatest diameter. They are transparent, with one or two vacuoles; contain often a somewhat granular protoplasm, and occur together, united two by two; or, if in active growth, in groups, of which seven is a very common number. These groups are derived from offshoots or buds from a single cell, which will be found somewhere near the middle, and can be identified by its greater size. The usual teaching as to the mode of propagation has been hitherto that this growth is effected by a true budding; but according to Dr. de Vaureal, the supposed budding is an optical delusion. He considers the utricle of yeast as allied to the spermogones of Tulasne. The nucleolar elements of the cell are spermatic; and being set free by the rupture of the cell-wall, produce new cells. This explanation would at all events account for the ready manner in which yeast germs are carried about by the air.

Schlossberger and many other chemists have determined the chemical composition of yeast. Schlossberger gives the mean of two analyses as follows [the elementary composition after removal of ash]:—

	Surface Yeast.	Sedimentary Yeast.
Carbon,	49·9	48·0
Hydrogen,	6·6	6·5
Nitrogen,	12·1	9·8
Oxygen,	31·4	35·7
[Ash,	2·5	3·5]

The ultimate principles contained in yeast appear to be, certain albuminoid substances, tyrosine, leucine [neuclein?], cellulose, and some other hydro-carbons, but the matter is not yet fully worked out.

The ash of yeast has been analysed by Mitscherlich, and Schutzenberger arranges his analyses as follows:—

	Surface Yeast.	Sediment Yeast.
Phosphoric acid,	41·8	39·5
Potash,	39·8	28·3
Soda,	...	...
Magnesium Phosphate ($Mg_2 2PO_4$),	16·8	22·6
Calcium Phosphate ($Ca_2 2PO_4$),	2·3	9·7

The researches of Ergol, Rees, Pasteur, and others have shown that there are a great variety of alcoholic ferments: the wine ferment is distinct in size and shape from the beer-yeast ferment; while the ferment of fruit-juice, again, differs in the figure of its cells from either; and to the various alcoholic ferments names have been given—*e.g.*, *Saccharomyces ellipsoideus*, *S. exiguus*, *S. conglomeratus*, *S. apiculatus*, &c. All of them, however, are of quite the same general type as yeast ferment.

§ 253. When liquids become sour, ropy, or putrid, in each case the change has been produced by a particular ferment. The *lactic acid ferment*, e.g., decomposes sugar into lactic acid; the *butyric acid ferment* attacks fatty matters, and separates in a free state butyric acid; and *putrid ferments*, by their avidity for oxygen, split up complex organic matters into a variety of substances. Of these ferments, the most important in reference to beer is the lactic acid ferment. In normal alcoholic fermentation, M. Pasteur has proved that there is not the smallest production of lactic acid, and when this does appear, it is certain that it has originated in and contaminated the yeast used. These ferments can be recognised by the microscope, and they should be looked for generally in the sediment. For the purpose of collecting the sediment of beers, wines, water, &c., the author has devised the following tube (fig. 43). The tube is of the capacity of a litre, and at the lower end is conical and open; on to this conical end is ground a glass cap, C, which is in point of fact a shallow cell about an inch in depth; P is a glass rod, the end of which fits easily into the narrow part of the tube, and is ground so as to make a perfect joint. The use of the tube is as follows:—The liquid under examination is placed in the tube closed by the cap, and the plunger P is removed; when the sediment has all collected in C, the plunger is very slowly and carefully inserted, so as to stopper the lower end of the tube; the cap may then be removed for microscopical examination.

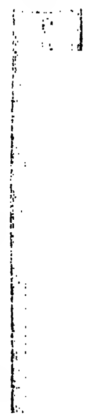

Fig. 43.

Fig. 44 is a representation, after Pasteur, of the ferments which characterise sour or turned beer.

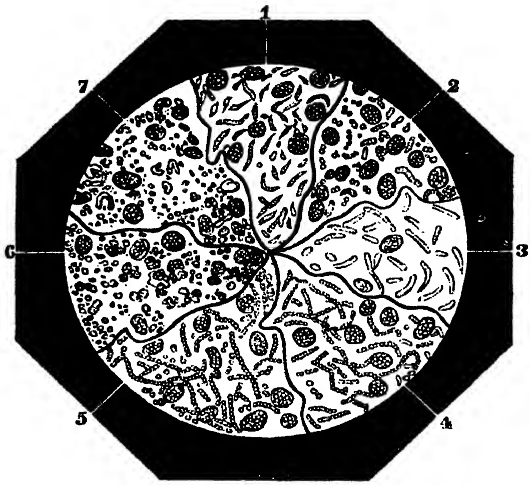

Fig. 44.

1. Turned beer—filaments simple or articulated into chains of different size; diameter $\frac{1}{15000}$ inch.
2. Lactic ferments of beer and wort—small, fine, and contracted in the middle; diameter a little greater than No. 1.
3. Ferments of putrid wort and beer—mobile filaments generally, which appear at the commencement of fermentation when it is slow; invariably the result of defective working.
4. Ferments of *viscous* wort and ropy beer, rare.
5. Pungent sour beer with acetic odour—chaplets of *Mycoderma aceti.*
6. A wort deposit.
7. Beer of a peculiar acidity—having a detestable taste and smell, generally found with No 1, but more to be feared than No. 1.

BEER.

§ 254. The most accurate definition of beer, as brewed in the present day, is that of a fermented saccharine infusion, to which has been added a wholesome bitter. The chief constituents of beer, stouts, and porters, are—

(1.) Water containing in solution (according to its origin) various salts. Distilled water is never used in brewing.
(2.) Alcohol.
(3.) Carbonic and acetic acids.
(4.) Malt extract, { Malt, sugar, dextrine, albuminous constituents, and ash.

(5.) Bitter principles, occasionally derived solely from the hop, but very commonly supplemented by so-called "hop substitutes." Samples of the latter examined by the author all contained "quassia," and portions of the following plants were identified—Calumba, chirata, gentian, and wormwood.

(6.) The ash derived from the water, the malt, and the bitters.

To these must be added volatile and essential oils, vegetable gelatine, glucinic acid derived from the sugars, lactic acid, and, in porters, caramel and assamar.

The general composition of the chief ingredients of beer may be gathered from the following table, taken from Mr. Watts' Dictionary:—

TABLE XXXVI.—SPECIAL EXAMINATION OF CERTAIN BEERS.

Name of Beer.	Malt Extract. Per cent.	Alcohol. Per cent.	Carbonic Acid. Per cent.	Water. Per cent.	Analysed by
London Porter, Barclay & Perkins, ...	6·0	5·4	0·16	88·44	Kaiser.
London Porter, ...	6·8	6·9	...	86·3	Balling.
,, ,, Berlin, . .	5·9	4·7	0·37	89·0	Ziurek.
Burton Ale, ...	14·5	5·9	...	79·6	Hoffmann.
Scotch Ale, Edinburgh, . .	10·9	8·5	0·15	80·45	Kaiser.
Ale, Berlin, ...	6·3	7·6	0·17	85·93	Ziurek.
Brussels Lambick, . . .	3·4	5·5	0·2	90·90	Kaiser.
,, Faro, ...	2·9	4·9	0·2	92·00	,,
Salvator Bier, Munich, . .	9·4	4·6	0·18	85·85	,,
Bock Bier, ,, . . .	9·2	4·2	0·17	86·49	,,
Bavarian Draught Beer (Schenk Bier, Munich), .	5·8	3·8	0·14	90·26	,,
Bavarian Store Beer (Lager Bier, Munich, 16 months old), ...	5·0	5·1	0·15	89·75	,,
Bavarian Store Beer, Munich,	3·9	4·3	0·16	91·64	,,
,, Draught Beer, Brunswick,	5·4	3·5	...	91·1	Otto.
Bavarian Beer (Waldschlösschen)	4·8	3·6	...	91·5	Fischer.
Prague Draught Beer, . .	6·9	2·4	...	90·7	Balling.
,, Town Beer (Stadt Bier),	10·9	3·9	...	85·2	,,
Sweet Beer, Brunswick, .	14·0	1·36	...	84·7	Otto.
Josty's Beer, Berlin, . .	2·6	2·6	0·5	94·3	Ziurek.
Werder's Brown Beer, Berlin,	3·1	2·3	0·3	94·2	,,
White Beer, Berlin, . .	5·7	1·9	0·6	91·8	,,
Bière Blanche de Louvain, .	3·0	4·0	...	93·0	Le Cambre.
Peterman (Louvain), . .	4·0	6·5	...	89·5	,,

The composition of beers, as a whole, varies in some degree according to the kind of ale or beer, according to the method of manufacture, and according to its age and preservation.

Pale Ale should be made from the finest and highest dried malt and the choicest hops, the bitter being in excess.

Mild Ale is a sweet, rather strong beer. *Table beer* is rarely sold—it is a weak watery ale.

Porter, as drunk in the metropolis, is a rather weak malt-liquor, coloured and flavoured with roasted malt. *Stout* is a richer and stronger description of porter.

The *German Beers* generally are fermented by sedimentary yeast, and are always, by reason of the after fermentation ("*Nachgährung*"), well charged with carbon dioxide. The lager, summer, bock, or export beers are separated from the winter beers only by the former being brewed from a richer wort, and containing more alcohol, as well as a greater percentage of malt extract.

Bavarian Beers in some degree derive their peculiar qualities from fermentation at a low temperature. They seldom contain more than two per cent. of alcohol, are only slightly bittered, have a fine aroma, and a peculiar flavour, said to be due to the solution of a minute fraction of the resinous matters used to caulk the casks.

Lambick and Faro Beers are made with unmalted wheat and barley malt. In fermentation the wort is self-impregnated, the process sometimes taking months, and being mostly of a bottom character. The beer contains a large quantity of lactic acid, and is very hard in consequence.

Of the constituents of beer, it will be necessary to notice fully the water, the malt extract, the bitters, and the ash.

§ 255. The *water used by the brewer* is mainly interesting to the analyst on account of the common salt held in solution, since in prosecutions for the addition of salt the defence generally is, that the latter is a natural component of the beer. Thus, Dr. Bottinger's analysis of the constituents of the water used at Messrs. Allsopp's brewery is as follows:—

	Per Gallon.
Chloride of sodium,	10·12
Sulphate of potash,	7·65
,, lime,	18·96
,, magnesia,	9·95
Carbonate of lime,	15·51
,, magnesia,	1·70
,, iron,	0·60
Silica,	0·79
	65·28

Messrs. Bass and Co.'s water (according to an old analysis of Cooper) contains chlorine equal to a little over 10 grains of common salt per gallon, and all published analyses of water used in breweries give quantities of salt under 14 grains per gallon. However, since breweries, as a rule, use hard spring water, it is quite possible for the water in particular localities to contain a much larger percentage of salt than the quantity mentioned above.

§ 256. *Malt Extract.*—The constituents of barley and also of malt are given in the following table; but of these it is the ash alone which will remain, comparatively speaking, unchanged; for by the action of mashing a very large portion of the dextrine and starch becomes changed into sugar.

TABLE XXXVII.—Composition of Barley and Malt.

	Barley.	Malt.		
	Air-dried.	Air-dried.	Kiln-dried, pale.	Kiln-dried, amber.
Produce of torrefaction, .	0·0	0·0	7·8	14·0
Dextrine, ...	5·6	8·0	6·6	10·2
Starch, ...	67 0	58·1	58·6	47·6
Sugar, ...	0·0	0·5	0·7	0·9
Cellulose, ...	9·6	14·4	10·8	11·5
Albuminous substances, .	12·1	13·6	10·4	10·5
Fatty substances, . .	2·6	2·2	2·4	2·6
Ash, &c., ...	3·1	3·2	2·7	2·7
	100·0	100·0	100·0	100·0

Barley contains dextrine, starch, albuminous substances, and a small quantity of fat, together with cellulose, and the ordinary saline constituents of seeds. Malt, varying a little in composition according to the heat of the final operations of the maltster, differs from barley in containing a small quantity of sugar (derived from transformation of a portion of the starch), rather more dextrine, and altogether less organic matter, the loss on malting being usually represented as—

Water,	6·00
Saline matter,	0·48
Organic matter,	12·52
	19·00

in 100 per cent. barley.

The constituents of barley are thus given by Oudemann:—

DRIED BARLEY.

Starch,	65·7
Dextrine,	5·5
Gluten insoluble in water, soluble in alcohol,	0·3
Soluble albuminous bodies coagulable by heat,	0·3
,, ,, not coagulable,	1·9
Albuminous bodies insoluble in water or in alcohol,	9·3
Fatty substances,	2·5
Cellulose,	9·4
Ash,	3·1
Lime, &c.,	2·0

According to Thomson, the following is the relative composition of the ash of malt and barley:—

	Barley.	Malt.
Potash,	16·00	14·54
Soda,	8·86	6·08
Lime,	3·23	3·89
Magnesia,	4·30	9·82
Ferric oxide,	0·83	1·59
Phosphoric acid, P_2O_5,	36·80	35·34
Sulphuric acid, (SO_3),	0·16	0·0
Chlorine,	0·15	Trace.
Silica,	29·67	28·74

Valentine and O'Sullivan have recently disputed the correctness of Oudemann's and the older analyses in the following points:—Oudemann finds from 5 to 8 per cent. of dextrine, Mr. O'Sullivan no dextrine at all; the small percentages of sugar generally quoted—viz., up to 1·0 per cent., Mr. O'Sullivan gives at from 16 to 20 per cent.; and the authors have compiled the following table, stating that each item has been estimated directly, and not by difference:—

Composition of Pale Malt.

		(1.)		(2.)
Starch, ...		44·15		45·13
Other carbo-hydrates (of which 60 to 70 per cent. consist of fermentable sugars), Inulin (?), and a small quantity of other bodies soluble in cold water, .		21·23		19·39
Cellular matter, . . .		11·57		10·09
Fat, ...		1·65		1·96
Albuminoids—				
(*a.*) Soluble in alcohol of specific gravity ·820, and in cold water, .	·63	...	·46	
(*b.*) Soluble in cold water and at 68°, . .	3·23	...	3·12	
(*c.*) Insoluble in cold water, but soluble at 68° to 70°, ...	2·37	...	1·36	
(*d.*) Insoluble at 68° to 70°, but soluble in cold water (albumen proper), . . .	·48	...	·37	
(*e.*) Insoluble in cold water and at 70°, . .	6·38	..	8·49	
		13·09		13·80
Ash, ...		2·60		1·92
Water, ...		5·83		7·47
		100·12		99·76

§ 257. *The Colouring-Matters of Malt.*—The colouring-matter of malt has been investigated by Sorby, and examined spectroscopically. The colour is of an orange yellow, and may be obtained from the hot water extract of malt, after having got rid of as much sugar and gum as possible. Ammonia colours it a deeper yellow, so does 50 per cent. sulphuric acid. There is no distinctive spectrum. A special test is to add citric acid to a watery or alcoholic solution, and then sodic hypochlorite. The watery solution under these circumstances becomes flesh-coloured, turbid, and after a time precipitates. The spectrum, according to Sorby, is moderately dark from D $\frac{1}{4}$ E to F $\frac{1}{2}$ G, clearer from there to F $\frac{3}{4}$ G, then moderately dark without estimable narrow bands; but in alcoholic solution, the solution remains clear, and there is a well-marked band at the yellow end of the green, which is at $4\frac{3}{4}$ of Sorby's scale (that is, between D $\frac{1}{4}$ E to D $\frac{5}{8}$ E); if the colour is deeper the band is more evident, and goes to D $\frac{2}{3}$ E. These appearances

are so characteristic that the colouring of malt in complex mixtures can be discovered by them. In barley the colour does not exist.

The carbonised or high-dried malt, used to colour porters and dark beers, contains at least two colouring-matters different from that just described. The one is orange-yellow, soluble in water and strong alcohol; it gives no flesh-coloured precipitate with sodic hypochlorite and citric acid, nor does it (like the hop colouring-matters) darken by oxidising agents; it is therefore probably a caramel. The other substance may be separated as follows:—The beer is evaporated to a small bulk, and precipitated by alcohol; the colour is thrown down, mixed with gum, and by redissolving and reprecipitating it can ultimately be obtained nearly pure. In aqueous solution it gives an orange-brown spectrum, which is very slightly shaded from D $\frac{1}{4}$ E, moderately dark to E and $\frac{1}{2}$ C, after that very dark.

A sugar, "maltose," is obtained by the action of malt extract on starch; it has a specific rotatory power of + 150°. The behaviour of maltose to Fehling's solution, and its method of estimation, is described at p. 116. It forms a hard, white, crystalline mass, consisting of needles, which lose their water in a current of air at 100°.

§ 258. *Beer Bitters.*—Beer, bittered by the hop alone, when precipitated by acetate of lead, filtered, and the excess of lead removed by hydric sulphide, gives a filtrate destitute of bitter taste; while, on the contrary, if it has a bitter taste, some bitter other than hop has been used. Whether such bitter is an adulteration or not, will depend altogether on the nature of the substance added; for since the repeal of the hop duty in 1862, and the consequent return of the trade to other bitters, anything harmless in the way of a bitter is perfectly legal. If, however, such poisons as picric acid, picrotoxin, or colchicine, should be found, there can be no difference of opinion as to the course the analyst should pursue.

With regard to these, picric acid has certainly been discovered, and picrotoxin is strongly suspected, but as yet the latter has not been proved to be a common adulterant. The so-called discovery of colchicine in beer appears to have been throughout a mistake. A sample of beer of unknown origin was found to contain a bitter amorphous substance, soluble in water and alcohol, and capable of separation from its acid watery solution by either chloroform or ether. Nitric acid of 1·48 dissolved it with a fine reddish colour, and a mixture of nitric and sulphuric acids turned it rose-red. H. Van Geldern* finds that the body

* *Arch. Pharm.*, 3, ix. 32.

which gives these reactions originates in the hop, and that the reactions are only produced in the presence of gelatine; and further, that a mixture of unadulterated hops and gelatine gives all the reactions of colchicine. This observation is quite as important to the toxicologist as to the food analyst.*

§ 259. *Hops.*—Hops are the catkins of the *Humulus lupulus*, and consist of imbricated scales enclosing the so-called nut. The scales themselves are covered with aromatic superficial glands, which are designated "yellow powder," or lupulin. Freed as far as possible from the lupulinic grains, the scales consist of astringent matter, chlorophyll, gum, colouring-matter, and ash. The lupulin itself, according to Dr. Yves, contains the following matters:—

Volatile Oil,	?
Tannin,	4·16
Extractive,	8·33
Bitter principle.	9·16
Wax,	10·00
Resin,	30·00
Lignin,	38·33
Loss,	·02
	100·00

This analysis does not include the oil of hops, which is a very important constituent of the hop, and may be obtained by distilling the fresh flowers or the lupulin.

The resin and bitter principle of the hop are to the brewer the most important constituents, its commercial value being directly dependent on them. According to some recent analyses made by Mr. Porter, the substances capable of solution in ether (viz., the oil, resin, and bitter principle) vary in different samples from 8·8 to a little over 17 per cent.†

Lupulite, or true Lupulin (a substance isolated by Lermer in 1863), can be obtained in rhombic prisms by treating fresh hops with four times their weight of ether, distilling the ether off, then adding to the extract alcohol of 90 per cent. (which leaves the wax undissolved), and again taking up the alcoholic extract with ether. The ethereal solution is repeatedly shaken with strong potash-lye to get rid of the resin, and lastly with pure

* Phospho-molybdic acid gives a *thick yellow* precipitate with lupuline. On adding ammonia, and placing in a watch-glass, the precipitate becomes surrounded by a blue zone. Colchicine behaves in a similar way.—*Zeitschrift für Analyt. Chemie*, 1880, p. 106.

† On the Examination of Hops, by W. E. Porter, F.C.S. *Analyst*, August, 1877; January, 1878.

water to take up the bitter matter. It is precipitated from the aqueous solution by sulphate of copper, the composition of the precipitate being $C_{16}H_{25}CuO_4$; and crystals are obtained by dissolving the precipitate in ether, decomposing with SH_2, and evaporating the ethereal filtrate in a stream of carbonic acid gas.

A principle very bitter, but not crystalline, can also be obtained by adding to the aqueous extract of the lupulin grains a little lime, and then treating with alcohol. The solution is to be evaporated, the mass treated with water, and the solution again evaporated to dryness. On washing this residue with ether, a white uncrystallisable, bitter principle—soluble in 20 parts of water, very soluble in alcohol, and but slightly so in ether—is obtained; it is probably a derivative of Lermer's lupulite.

Lermer's Lupulite crystallises in glittering, rhombic, brittle prisms, tasteless in themselves, but with a very bitter flavour, and an acid reaction when dissolved in alcohol. They are insoluble in water, but dissolve easily in alcohol, ether, chloroform, bisulphide of carbon, benzole, and turpentine; exposed to the air, they soon become yellow and partly amorphous.

TABLE XXXVIII.—CONSTITUENTS OF THE ASH OF HOP CONES.

	Way and Ogston.			E. Watts.
	Bentley Variety.	Golding Variety.	Grape Variety.	Grape Variety.
Potash,	11·98	24·88	25·56	19·41
Soda,	...	...	...	0·70
Lime,	17·93	21·59	18·47	14·15
Magnesia,	5·94	4·69	5·27	5·34
Alumina,	...	...	...	1·18
Ferric Oxide,	1·86	1·75	1·41	2·71
Sulphuric Acid,	7·01	7·27	11·68	8·28
Chlorine,	...	...	...	2·26
Silica,	22·97	19·71	9·99	17·88
Carbonic Acid,	5·44	2·17	4·54	11·01
Phosphoric Acid,	21·38	14·47	17·58	14·64
Chloride of Potassium,	5·45	...	4·34	...
,, Sodium,	...	3·42	0·12	...
Charcoal and Loss,	...	...	...	2·44
	99·96	99·95	98·96	100·00
Ash per cent. of Dry Hops,	8·07	5·95	7·21	...
,, ,, Fresh ,,	7·27	5·22	6·22	6·5

The ash of the hop differs but little from the ashes of foliar organs generally, the relative proportion of each constituent varying within somewhat wide limits, according to the particular variety. (See accompanying table.)

Oil of Hops, according to the researches of Wagner, consists chiefly of an oxygen-holding oil, $C_{10}H_{18}O$, containing in solution a camphor boiling at 175°. The specific gravity of the oil itself is 0·968. It begins to boil at 125°, and successive portions can be separated by fractional distillation, the last passing over at 235°; one-sixth distils over between 125° and 175°, and is of a pale colour and quite clear; about half passes over between 175° and 225°, and is also very clear; but the remainder is yellow, and the residue in the retort has the appearance of a brown turpentine.

The crude oil is brownish-yellow, and very sparingly soluble in water, one part requiring more than 600 times its weight for complete solution. It does not contain sulphur, as previously asserted by Payen and Chevallier, nor does it reduce ammoniacal solution of silver. Oxidation by nitric acid produces valerianic acid and a yellow acid resin; if dropped on melted caustic potash, valerianate, carbonate of potash, and a hydrocarbon are the results. The oil appears to be neither narcotic nor poisonous, twenty drops having had no action whatever on a kitten (*W. Keil*); but the wonderful preservative properties ascribed to it by older writers are very problematical.

M. Issleib has recently made a careful examination of the bitter principles of the hop. His method of separation was to extract with cold water, and then to treat the cold extract with animal charcoal, exhausting the latter after drying with 90 per cent. alcohol. This gave a yellow solution, from which a brown resin was precipitated on concentration, leaving in solution the bitter principle and another substance (C). The bitter may be removed by ether, and is pale yellow, amorphous, non-nitrogenous, and slightly acid, and is dissolved by alkalies with the production of a fine yellow colour. He ascribes to it the composition of $C_{29}H_{46}O_{10}$, and states that it splits up under the influence of sulphuric acid, thus—

$$\underset{\text{Bitter Principle.}}{2C_{29}H_{46}O_{10}} + 3H_2O = \underset{\text{Lupuliretin.}}{C_{10}H_{16}O_4} + \underset{\text{Lupulic Acid.}}{C_{40}H_{82}O_{19}}$$

The resin has the composition of $C_{10}H_{24}O_{31}$, and is presumed to be formed by the oxidation of oil of hops; lastly, the substance C is considered to be an oxidation product of the oil of hops, and has the composition of $C_{10}H_{18}O_6$.*

* *Arch. Pharm.*, [3],16,345–363; *Journ. Chem. Soc.*, March, 1881.

A few other bitter principles, some of which have actually been found, and the remainder are supposed to exist, may be now conveniently described. (For *Picrotoxin* and *Colchicine* the reader is referred to the second volume of this work.)*

§ 260. *Absynthin*, $C_{40}H_{28}O_8HO$.—The bitter principle of wormwood, *Artemisia absynthium*. It may be extracted from the hot aqueous extract of wormwood by precipitation with tannic acid, evaporating the tannate to dryness with oxide of lead, and extracting the dried residue by alcohol, and subsequent purification with animal charcoal. Absynthin dissolves easily in alcohol and ether, with difficulty in hot water, and is scarcely soluble in cold. When obtained from alcoholic solution it is usually in the form of pale-yellow drops, which gradually become crystalline; it has a peculiar odour and extremely bitter taste, and its reaction is neutral. It reduces a hot ammoniacal solution of silver nitrate, but an alkaline tartrate of copper solution remains unchanged by it. It is dissolved by caustic potash with the production of a brown colour. Concentrated sulphuric acid produces first a brown colour, passing into a green-blue; as water is added, the colour becomes darker, until grey flocculent particles are separated. Boiling with dilute acids produces resinous products, but no sugar.

The bitter principle, according to some observers, is a direct cerebral excitant; according to others, a pure tonic. It is used occasionally in medicine, in doses from ½ grain to 2 grains, and the herb producing it is officinal in the Continental pharmacopœias.†

§ 261. *Aloin* — $C_{16}H_{18}O_7$ (TILDEN), $C_{17}H_{18}O_7$ (STENHOUSE), $C_{15}H_{16}O_7$ (E. SCHMIDT)—may be obtained by treating aloes with dilute sulphuric acid, removing the deposit of resin, and evaporating to a syrup. The crystals thus obtained are yellow needles, soluble in water and alcohol, and possessing a bitter taste. The amount of crystallisation water varies from 5·89 to 14·29 per

* *Bibliography.*

LERMER—*Dingl. Polytech. Journ.*, clxix. 54; *Viertelj. Pract. Pharm.*, xii. 505.

PAREIRA'S "Materia Medica."

HUSEMANN.—"Die Pflanzenstoffe," &c.

PAYEN and CHEVALLIER.—*Journ. Pharm.*, [2], viii. 214, 533.

PERSONNE.—*Journ. Pharm.*, [3], xxvj. 241, 329; xxvj. 22.

† KROMAYER.—*Arch. Pharm.*, [3], cviii. 129.

LEONARDI.—Osservazioni ed esperienze del Dott. Lupis sopra la virtù antifebrile dell estratto amarissimo d'assenzio, &c. Milano, 1828.

LUCK.—*Ann. Chem. Pharm.*, liv. 112; lxxviii. 87.

RIGHINI.—*Journ. Chim. Méd.*, xix. 383; *Journ. Chim. Méd.*, 2e ser., ix. 383.

cent.; if anhydrous, the melting point of the crystals is from 70° to 80° [146° to 148°F.]; if hydrous, sulphuric acid colours it first red, then orange, and it is dissolved by caustic potash with the production of a purple-red colour. The action of nitric acid produces chrysammic, picric, and oxalic acids, with the addition of carbonic anhydride; that of zinc dust, methylanthracene and anthraquinone.*

§ 262. *Cnicin*, $C_{42}H_{56}O_{15}$, was discovered by Nativelle in the leaves of the *Cnicus benedictus;* it is found also in the *Centaurea calcitrapa*, and in other composite plants. It forms transparent silky crystals, neutral, without smell, of very bitter taste, melting at a high temperature, but not subliming. Its solution turns the plane of polarisation to the right $[\alpha]\ r = 130°68$. It is scarcely soluble in cold water, more so in boiling, soluble in all proportions in alcohol and wood spirit, almost insoluble in ether. Cold sulphuric acid gives with cnicin a red solution, becoming violet on the addition of water, and yellow on the addition of ammonia. Cold concentrated hydrochloric acid dissolves it with the production of a green colour; on heating, brown drops separate, which solidify into a yellow resin.†

§ 263. *Daphnin*, $C_{31}H_{38}O_{19}$, a crystalline principle discovered by Vauquelin, 1817, in the bark of the *Daphne alpina*, L., and *D. mezereum*, L. It forms long rectangular prisms, or fine needles, and crystallises with four atoms of water. Its reaction is neutral, its taste bitter. When anhydrous it melts at about 200° to a colourless fluid, which again becomes crystalline on cooling; if the heat is continued, it sublimes as daphnetin, $C_{19}H_{14}O_9$. This substance presents itself in fine, colourless, rhombic prisms, melt-

* *Bibliography.*
GROVES.—*Pharm. Journ. Trans.*, xvj. 128; *Journ. Pharm.*, [3], xxxi. 367.
FLUCKIGER.—"Year-Book of Pharmacy," 1872.
HANBURY and FLUCKIGER.—"Pharmacographia," 1876.
KOSMANN.—*Journ. Pharm.*, [3], xl. 177; *Bull. Soc. Chim.*, v. 530.
ORLOWSKY.—*Zeitsch. Analyt. Chem.*, v. 309.
ROBIQUET.—*Journ. Pharm.*, [3], x. 173; xxix. 241.
ROCHLEDER and CZUMPELIK.—*Wien. Akad. Ber.*, xliv. [2], 493; xlvii. [2], 119.
SCHMIDT.—*Arch. Pharm.* [3], vi. 496-509.
SCHROFF.—*N. Repert. Pharm.*, ii. 49.
SMITH, T. and H.—*Chem. Gaz.*, 1851, 107; *Journ. Pharm.* [3], xix. 275.
STENHOUSE.—*Phil. Mag. Journ.*, xxxvij. 481; *Ann. Chem. Pharm.*, lxxvij. 208.
TILDEN.—*Pharm. Journ. Trans.*, [3], vj. 208-210.
† BOUCHARDAT.—*Compt. Rend.*, xviii. 299.
DESSAIGNES and CHAUTARD.—*Journ. Pharm.*, [3], xxi. 26.
HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
NATIVELLE.—*Journ. Chim. Méd.*, xxi. 69.
SCRIBE.—*Compt. Rend.*, xv. 802.

ing about 250° ; it has a bitter taste, with a weak acid reaction, and is easily soluble in boiling water, with the production of a yellow colour; it dissolves also in boiling alcohol, but is very little soluble in ether.

Daphnin dissolves slightly in cold water, easily in hot; it is also very soluble in hot alcohol, but is not dissolved at all by ether. In solutions of the caustic and the carbonated alkalies it dissolves with the production of a yellow colour and is also easily soluble in acetic acid. On boiling with a dilute acid, daphnin breaks up into daphnetin and sugar, and emulsin and fermentation with yeast have a similar effect. An aqueous solution of chloride of iron produces, when cold, a blue colour, and if the liquid is boiled, a dark yellow precipitate. Nitric acid colours it red.*

§ 264. *Gentianin*, $C_{14}H_{10}O_5$, discovered by Henry and Caventou in 1821, but first prepared pure by Trommsdorff, is found, like gentiopicrin, in the root of the *Gentiana lutea*, L. It forms long, pale-yellow, silky needles, without smell or taste, which may be sublimed above 300° without decomposition. Its solubility, according to Leconte, is as follows:—1 part requires of cold water 5000 parts, of boiling 3850 parts; of cold absolute alcohol 455 parts, of boiling 62·5 parts; of cold ether 2000 parts, for solution. Concentrated sulphuric acid dissolves it with a yellow colour; on dilution with water it separates unchanged; on being boiled with dilute sulphuric acid there is no change. If treated with pure nitric acid (1·43 specific gravity), a dark-green solution is obtained, and on adding water carefully dinitro-gentianin, $C_{14}H_8(NO_2)_2O_5 + H_2O$ separates out as a green powder. If similarly treated with strong nitric acid, and subsequent addition of water to the solution, yellow microscopical prisms are separated, probably *trinitro-gentianin*. Gentianin reduces nitrate of silver.†

§ 265. *Gentiopicrin*, $C_{20}H_{30}O_{12}$, first prepared pure by Kromayer in 1862, is a glucoside found in the fresh root of the *Gentiana lutea*. It crystallises in colourless needles, with one atom of water

* *Bibliography.*
GMELIN and BÄR.—*Schweigg. Journ.*, xxxv. 1.
HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
ROCHLEDER.—*Journ. Pract. Chem.*, xc. 442.
VAUQUELIN.—*Ann. Chim.*, lxxxiv. 174.
ZWENGER.—*Ann. Chem. Pharm.*, cxv. 1.

† BAUMERT.—*Ann. Chem. Pharm.*, lxii. 106.
HENRY and CAVENTOU.—*Journ. Pharm.* [2], vii. 173.
HUSEMANN.—"Die Pflanzenstoffe." Berlin 1871.
LECONTE.—*Journ. Pharm.*, [2], xxiii. 465.
TROMMSDORFF.—*Ann. Chem. Pharm.*, xxi. 134.

of crystallisation. The crystals effloresce in the air, and lose their transparency, becoming white and opaque. The anhydrous crystals melt between 120° and 125° to a brown fluid, which coagulates amorphously, and at higher temperatures is fully destroyed. Water dissolves it easily, but it is insoluble in absolute alcohol and in ether, though, on the other hand, weak alcohol is an excellent solvent for it. One of the best tests for its presence is the action of concentrated sulphuric acid, giving in the cold a colourless solution, but producing with slight warming a carmine-red colour, and precipitating on the addition of water in grey flocks. It reduces an ammoniacal solution of silver nitrate, and in boiling with dilute sulphuric acid splits up into sugar and gentiogenin.

Gentiogenin, $C_{14}H_{16}O_5$, is an amorphous, yellow-brown powder, of neutral reaction and bitter taste, not easily soluble in cold water, but dissolving readily in alcohol and ether.*

§ 266. *Menyanthin*, $C_{30}H_{46}O_4$, a glucoside obtained pure by Ludwig and Kromayer in 1861, from the *Menyanthes trifoliata*, L. As hitherto prepared, menyanthin is an amorphous, terebinthinate mass, becoming slowly solid on drying over sulphuric acid. It has a neutral reaction, and its taste is strongly and purely bitter. It softens at 60° to 65°, and melts at 10° to 15° to a thin, clear fluid, which again solidifies to a hard transparent mass; by stronger heating it is entirely destroyed. Concentrated sulphuric acid gives with it a yellow-brown colour, which on standing becomes violet-red, and grey flocks are separated on the addition of water. By heating with dilute sulphuric acid it splits up into sugar and menyanthol.

Menyanthol is an oil having an acid reaction, and an odour like that of oil of almonds; it is changed by the air (as well as by melting with potash) into a crystalline acid capable of being sublimed.†

§ 267. *Quassiin*, $C_{10}H_{12}O_3$, a bitter principle, discovered in 1835 by Winckler, in the bark of the *Quassia amara*, L., and *Picræna excelsa*, L. It forms white, opaque, glittering crystals, without odour, and of extremely bitter taste. On heating, it melts and solidifies as a transparent yellow mass; at decomposition temperatures it burns like resin, if exposed to the air. Tannic acid precipitates it from an alcoholic solution in thick, white flocks;

* *Bibliography.*

HUSEMANN.—"Die Pflanzenstoffe."

KROMAYER.—*Arch. Pharm.* [2], cx. 27.

† HUSEMANN.—Die Pflanzenstoffe. Berlin, 1871.

KROMAYER.—*Arch. Pharm.* [2], cxxiv. 37.

LUDWIG and KROMAYER.—*Arch. Pharm.* [2], cviii. 263.

cold concentrated sulphuric acid dissolves it, without the production of colour; and on dilution with water it is apparently precipitated without change.*

§ 268. *The Ash of Beer.*—The ash of beer contains the mineral constituents that previously existed partly in the water, partly in the hop, and partly in the malt used. It would appear that the ferric oxide, a certain proportion of phosphoric acid, a small portion of the lime and magnesia, with a great part of the silica, remain undissolved, and do not pass into the beer; the rest are dissolved.

The following table gives the average composition of the beer ash of commerce:—

	Beer Ash.
Potash,	37·22
Soda,	8·04
Lime,	1·93
Magnesia,	5·51
Iron oxide,	traces
Sulphuric acid,	1·44
Phosphoric acid,	32·09
Chlorine,	2·91
Silica,	10·82

The table on next page may be also useful, showing analyses of ash by Walz and Dickson ("Dictionary of Chemistry, Arts, and Manufactures," edited by Vincent).

§ 269. *Analysis of Beer.*—The ordinary full analysis of beer determines—

(1.) The alcohol.
(2.) The carbonic acid.
(3.) The volatile and fixed acids.
(4.) The percentage of malt extract, and, if necessary, its composition.
(5.) The hop resin and glycerine.
(6.) The nature of the bitter used.
(7.) The general composition of the ash, and especially its chlorides.

(1.) *The alcohol* is found most accurately by the distillation process described at p. 373, but it is often determined in the following manner:—Shake up the beer in a flask, so as to

* *Bibliography.*

HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
WIGGERS.—*Ann. Chem. Pharm.*, xxi. 40.
WINCKLER.—*Repert. Pharm.*, xxi. 40.

TABLE XXXIX.—ASH OF BEERS.

	London Beer.	Munich Beer.	Speyer Beer.	Scotch Ale, 14 Samples.	Scotch Porter, 2 Samples.	Dublin Porter, 2 Samples.	London Porter, 5 Samples.
Potash,	38·35	36·58	37·68	3·2 — 29·8	18·9 — 20·9	21·4 — 32·0	4·9 — 31·1
Soda,	7·68	9·83	6·50	20·9 — 38·5	33·8 — 38·8	24·0 — 42·7	21·8 — 50·8
Lime,	2·45	1·48	2·98	0·2 — 2·0	1·3 — 1·6	0·8 — 1·5	0·8 — 6·9
Magnesia,	3·78	5·64	4·66	0·1 — 5·6	0·2 — 1·4	0·2 — 1·2	0·1 — 1·2
Sulphuric Acid,	1·36	1·68	2·56	1·6 — 19·2	2·2 — 6·4	2·8 — 10·1	1·6 — 12·2
Chlorine,	2·75	3·14	2·14	4·3 — 18·25	7·4 — 11·4	6·9 — 10·1	6·5 — 14·5
Silica,	9·87	9·96	10·29	4·6 — 19·1	13·3 — 18·6	6·9 — 19·7	8·25 — 19·7
Phosphoric Acid,	33·76	31·69	33·19	6·0 — 25·7	12·2 — 18·8	7·9 — 20·0	9·3 — 20·6
	100·00	100·00	100·00				

deprive it of as much carbonic acid as possible, then take the specific gravity at 15°·5, and boil a third of the beer away in an open beaker. To make up the boiled beer to exactly the original quality again, take the specific gravity, and calculate as described at p. 379.

(2.) *The carbonic acid* which the beer holds dissolved is most readily estimated by placing 100 cc. (or any convenient quantity) in a flask in connection with the Fox-Lane mercury pump described at p. 72; collecting the gases, and estimating the carbon dioxide in the usual way by absorbing it by caustic potash, and measuring the volume of gas before and after absorption. Another method is as follows:—A flask provided with a caoutchouc stopper, and carrying a tube twice bent at right angles, is connected with a smaller flask, containing strong ammonia water, into which the tube dips. This second flask must also carry a caoutchouc stopper, which should be doubly perforated, the one hole for the tube already mentioned, the other provided with a short, wide tube, packed with glass wool moistened with ammonia water. The beer must first be gently warmed and ultimately boiled, when the whole of the carbonic acid is absorbed by the ammonia. A sufficient quantity of a solution of calcium chloride is now added, the liquid boiled until all free ammonia is expelled, and the calcium carbonate thrown on a filter and washed. Lastly, the washed calcium carbonate is dissolved in either standard or decinormal acid, according to the quantity, a little cochineal solution is added, and the acid titrated back. 2 cc. of decinormal acid equal 10 mgrms. of carbonate of lime, or 4·4 mgrms. of CO_2. This simple process is applicable to all liquids from which carbonic anhydride can be expelled by boiling.

(3.) *Volatile and Fixed Acids.*—The acetic acid is obtained by distilling the beer nearly to dryness, and estimating the acidity of the filtrate by decinormal solution of soda. Should the residue in the flask or retort be still acid, a little water should be added, and the distillation again continued to dryness; any acid now remaining is certain to be a fixed acid, probably lactic. It may be estimated by titration, and returned as lactic. The equivalent of anhydrous lactic acid is 90; hence 1 cc. of d. n. soda = 9 mgrms. of lactic acid. Should it be specially necessary to determine the percentage of lactic acid, a sufficient quantity of beer—say 300 cc.—is taken, evaporated to a small bulk, diluted with water, filtered, and mixed with a little sulphuric acid; pure carbonate of baryta is now added, and the whole warmed on the water-bath for some time. The liquid is then freed from the precipitate of sulphate of baryta by filtration, and the pre-

cipitate well washed with hot water. This filtrate is evaporated to a syrup, and treated, when cold, in a tube or separating-funnel with a mixture of one part of sulphuric acid, one of water, one of alcohol, and ten of ether; the ethereal layer is separated in the usual way, and evaporated. The lactic acid thus obtained is still impure, and it is best to dissolve in water, saturate with freshly-precipitated carbonate of zinc, and estimate as zinc lactate, the latter containing 54·49 per cent. of anhydrous lactic acid. In most cases, however, the error will not be great, if the total acidity of the beer is taken directly without distillation, and returned as acetic acid.

(4.) *The Malt Extract.*—The extract of beer can be determined by evaporating down a carefully measured quantity, and weighing the dry residue. In order to do this with any approach to accuracy, the smallest possible quantity should be taken—5 cc. or 5 grms. is quite sufficient. This small quantity, spread out as a thin film on the bottom of a tolerably capacious platinum dish, can be thoroughly dried over the water-bath in two or three hours, while if such quantities as 25 cc., 50 cc., or 100 cc. are taken, to get the extract completely dry is very tedious, and usually requires a higher temperature than 100°. It is, however, found in practice much more convenient to dispense with this drying altogether, the alcohol and carbonic acid being driven off, as before described, the beer made up to its first bulk, the specific gravity taken, and the amount of malt extract determined by the aid of the following tables. If the beer has been distilled, the residue in the retort or flask can be made up to the original bulk, brought to the proper temperature, and treated as just described.

The alcoholic strength, the acetic acid, and the amount of malt extract being known, the analyst can now give a fairly approximate estimate of the amount of malt originally used in the brewing of the beer. To do this it is necessary to calculate the "original gravity" of the beer. The specific gravity of the alcoholic distillate (or, if an indirect process has been used, the specific gravity of the alcoholic strength) subtracted from 1000, gives a number called the "spirit indication." The degrees of gravity lost are then ascertained by the aid of the following tables, using the first if the beer has been distilled, and the second if the evaporating process has been used. The degrees of gravity thus found are added to the specific gravity of the boiled beer, and the number thus obtained is called "the original gravity of the wort." On reference to Table XL., the amount of malt extract is determined, which corresponds to this original gravity.

TABLE XL.—SPECIFIC GRAVITY AND STRENGTH OF MALT EXTRACT.

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0000	0,000	1,0047	1,175	1,0094	2,350	1,0141	3,525
1,0001	025	48	200	95	375	142	550
2	050	49	225	96	400	143	575
3	075	1,0050	250	97	425	144	600
4	100	51	275	98	450	145	625
5	125	52	300	99	475	146	650
6	150	53	325	1,0100	500	147	675
7	175	54	350	101	525	148	700
8	200	55	375	102	550	149	725
9	225	56	400	103	575	1,0150	750
1,0010	250	57	425	104	600	151	775
11	275	58	450	105	625	152	800
12	300	59	475	106	650	153	825
13	325	1,0060	500	107	675	154	850
14	350	61	525	108	700	155	875
15	375	62	550	109	725	156	900
16	400	63	575	1,0110	750	157	925
17	425	64	600	111	775	158	950
18	450	65	625	112	800	159	975
19	475	66	650	113	825	1,0160	4,000
1,0020	500	67	675	114	850	161	025
21	525	68	700	115	875	162	050
22	550	69	725	116	900	163	075
23	575	1,0070	750	117	925	164	100
24	600	71	775	118	950	165	125
25	625	72	800	119	975	166	150
26	650	73	825	1,0120	3,000	167	175
27	675	74	850	121	025	168	200
28	700	75	875	122	050	169	225
29	725	76	900	123	075	1,0170	250
1,0030	750	77	925	124	100	171	275
31	775	78	950	125	125	172	300
32	800	79	975	126	150	173	325
33	825	1,0080	2,000	127	175	174	350
34	850	81	025	128	200	175	375
35	875	82	050	129	225	176	400
36	900	83	075	1,0130	250	177	425
37	925	84	100	131	275	178	450
38	950	85	125	132	300	179	475
39	975	86	150	133	325	1,0180	500
1,0040	1,000	87	175	134	350	181	525
41	025	88	200	135	375	182	550
42	050	89	225	136	400	183	575
43	075	1,0090	250	137	425	184	600
44	100	91	275	138	450	185	625
45	125	92	300	139	475	186	650
46	150	93	325	1,0140	500	187	675

TABLE XL.—*Continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0188	4,700	1,0235	5,875	1,0282	7,024	1,0329	8,170
189	725	236	900	283	048	1,0330	195
1,0190	750	237	925	284	073	331	219
191	775	238	950	285	097	332	244
192	800	239	975	286	122	333	260
193	825	1,0240	6,000	287	146	334	292
194	850	241	024	288	170	335	316
195	875	242	048	289	195	336	341
196	900	243	073	1,0290	219	337	365
197	925	244	097	291	244	338	389
198	950	245	122	292	268	339	413
199	975	246	146	293	292	1,0340	438
1,0200	5,000	247	170	294	316	341	463
201	025	248	195	295	341	342	488
202	050	249	219	296	365	343	512
203	075	1,0250	244	297	389	344	536
204	100	251	268	298	413	345	560
205	125	252	292	299	438	346	584
206	150	253	316	1,0300	463	347	609
207	175	254	341	301	488	348	633
208	200	255	365	302	512	349	657
209	225	256	389	303	536	1,0350	681
1,0210	250	257	413	304	560	351	706
211	275	258	438	305	584	352	731
212	300	259	463	306	609	353	756
213	325	1,0260	488	307	633	354	780
214	350	261	512	308	657	355	804
215	375	262	536	309	681	356	028
216	400	263	560	1,0310	706	357	853
217	425	264	584	311	731	358	877
218	450	265	609	312	756	359	901
219	475	266	633	313	780	1,0360	925
1,0220	500	267	657	314	804	361	950
221	525	268	681	315	828	362	975
222	550	269	706	316	853	363	9,000
223	575	1,0270	731	317	877	364	024
224	600	271	756	318	901	365	048
225	625	272	780	319	925	366	073
226	650	273	804	1,0320	950	367	097
227	675	274	828	321	975	368	122
228	700	275	853	322	8,000	369	146
229	725	276	877	323	024	1,0370	170
1,0230	750	277	901	324	048	371	195
231	775	278	925	325	073	372	219
232	800	279	950	326	097	373	244
233	825	1,0280	975	327	122	374	268
234	850	281	7,000	328	146	375	292

TABLE XI.—*Continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract
1,0376	9,316	1,0423	10,452	1,0470	11,571	1,0517	12,690
377	341	424	476	471	595	518	714
378	365	425	500	472	619	519	738
379	389	426	523	473	642	1,0520	761
1,0380	413	427	547	474	666	521	785
381	438	428	571	475	690	522	809
382	463	429	595	476	714	523	833
383	488	1,0430	619	477	738	524	857
384	512	431	642	478	761	525	881
385	536	432	666	479	785	526	904
386	560	433	690	1,0480	809	527	928
387	584	434	714	481	833	528	952
388	609	435	738	482	857	529	976
389	633	436	761	483	881	1,0530	13,000
1,0390	657	437	785	484	904	531	023
391	681	438	809	485	928	532	047
392	706	439	833	486	952	533	071
393	731	1,0440	857	487	986	534	095
394	756	441	881	488	12,000	535	119
395	780	442	904	489	023	536	142
396	804	443	928	1,0490	047	537	166
397	828	444	952	491	071	538	190
398	853	445	976	492	095	539	214
399	877	446	11,000	493	119	1,0540	238
1,0400	901	447	023	494	142	541	261
401	925	448	047	495	166	542	285
402	950	449	071	496	190	543	309
403	975	1,0450	095	497	214	544	333
404	10,000	451	119	498	238	545	357
405	023	452	142	499	261	546	381
406	047	453	166	1,0500	285	547	405
407	071	454	190	501	309	548	428
408	095	455	214	502	333	549	452
409	119	456	238	503	357	1,0550	476
1,0410	142	457	261	504	381	551	500
411	166	458	285	505	404	552	523
412	190	459	309	506	428	553	547
413	214	1,0460	333	507	452	554	571
414	238	461	357	508	476	555	595
415	261	462	381	509	500	556	619
416	285	463	404	1,0510	523	557	642
417	309	464	428	511	547	558	666
418	333	465	452	512	571	559	690
419	357	466	476	513	595	1,0560	714
1,0420	381	467	500	514	619	561	738
421	404	468	523	515	642	562	761
422	428	469	547	516	666	563	785

TABLE XL.—*Continued.*

Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.	Specific Gravity.	Malt Extract.
1,0564	13,809	1,0604	14,761	1,0643	15,674	1,0682	16,581
565	833	605	785	644	697	683	604
566	857	606	809	645	721	684	627
567	881	607	833	646	744	685	650
568	904	608	857	647	767	686	674
569	928	609	881	648	790	687	697
1,0570	952	1,0610	904	649	814	688	721
571	976	611	928	1,0650	837	689	744
572	14,000	612	952	651	860	1,0690	767
573	023	613	976	652	883	691	790
574	047	614	15,000	653	907	692	814
575	071	615	023	654	930	693	837
576	095	616	046	655	953	694	860
577	119	617	070	656	976	695	883
578	142	618	093	657	16,000	696	907
579	166	619	116	658	023	697	930
1,0580	190	1,0620	139	659	046	698	953
581	214	621	162	1,0660	070	699	976
582	238	622	186	661	093	1,0700	17,000
583	261	623	209	662	116	701	022
584	285	624	232	663	139	702	045
585	309	625	255	664	162	703	067
586	333	626	278	665	186	704	090
587	357	627	302	666	209	705	113
588	381	628	325	667	232	706	136
589	404	629	348	668	255	707	158
1,0590	428	1,0630	371	669	278	708	181
591	452	631	395	1,0670	302	709	204
592	476	632	418	671	325	1,0710	227
593	500	633	441	672	348	711	250
594	523	634	464	673	371	712	272
595	547	635	488	674	395	713	295
596	571	636	511	675	418	714	318
597	595	637	534	676	441	715	340
598	619	638	557	677	464	716	363
599	642	639	581	678	488	717	386
1,0600	666	1,0640	604	679	511	718	409
601	690	641	627	1,0680	534	719	431
602	714	642	650	681	557	1,0720	17,454
603	738						

TABLE XLI.—For Use if the Distillation Process has been Used.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0·0	0·3	0·6	0·9	1·2	1·5	1·8	2·1	2·4	2·7
1	3·0	3·3	3·7	4·1	4·4	4·8	5·1	5·5	5·9	6·2
2	6·6	7·0	7·4	7·8	8·2	8·6	9·0	9·4	9·8	10·2
3	10·7	11·1	11·5	12·0	12·4	12·9	13·3	13·8	14·2	14·7
4	15·1	15·5	16·0	16·4	16·8	17·3	17·7	18·2	18·6	19·1
5	19·5	19·9	20·4	20·9	21·3	21·8	22·2	22·7	23·1	23·6
6	24·1	24·6	25·0	25·5	26·0	26·4	26·9	27·4	27·8	28·3
7	28·8	29·2	29·7	30·2	30·7	31·2	31·7	32·2	32·7	33·2
8	33·7	34·3	34·8	35·4	35·9	36·5	37·0	37·5	38·0	38·6
9	39·1	39·7	40·2	40·7	41·2	41·7	42·2	42·7	43·2	43·7
10	44·2	44·7	45·1	45·6	46·0	46·5	47·0	47·5	48·0	48·5
11	49·0	49·6	50·1	50·6	51·2	51·7	52·2	52·7	53·3	53·8
12	54·3	54·9	55·4	55·9	56·4	56·9	57·4	57·9	58·4	58·9
13	59·6	60·0	60·5	61·1	61·6	62·2	62·7	63·3	63·8	64·3
14	64·8	65·4	65·9	66·5	67·1	67·6	68·2	68·7	69·3	69·9
15	70·5	...	...	...	...	...	...	...	...	...

TABLE XLII.—For Use if the Evaporation Process is Adopted.

Degrees of Spirit Indication.	·0	·1	·2	·3	·4	·5	·6	·7	·8	·9
0	0	0·3	0·7	1·0	1·4	1·7	2·1	2·4	2·8	3·1
1	3·5	3·8	4·2	4·6	5·0	5·4	5·8	6·2	6·6	7·0
2	7·4	7·8	8·2	8·7	9·1	9·5	9·9	10·3	10·7	11·1
3	11·5	11·9	12·4	12·8	13·2	13·6	14·0	14·4	14·8	15·3
4	15·8	16·2	16·6	17·0	17·4	17·9	18·4	18·8	19·3	19·8
5	20·3	20·7	21·2	21·6	22·1	22·5	23·0	23·4	23·9	24·3
6	24·8	25·2	25·6	26·1	26·6	27·0	27·5	28·6	28·5	29·0
7	29·5	30·0	30·4	30·9	31·3	31·8	32·3	32·8	33·3	33·8
8	34·3	34·9	35·5	36·0	36·6	37·1	37·7	38·3	38·8	39·4
9	40·0	40·5	41·0	41·5	42·0	42·5	43·0	43·5	44·0	44·4
10	44·9	45·4	46·0	46·5	47·1	47·6	48·2	48·7	49·3	49·3
11	50·3	50·9	51·4	51·9	52·5	53·0	53·5	54·0	54·5	55·0
12	55·6	56·2	56·7	57·3	57·8	58·3	58·9	59·4	59·9	60·5
13	61·0	61·6	62·1	62·7	63·2	63·8	64·3	64·9	65·4	66·0
14	66·5	67·0	67·6	68·1	68·7	69·2	69·8	70·4	70·9	71·4
15	72·0	...	...	...	...	...	...	...	...	...

TABLE XLIII.—FOR ASCERTAINING THE VALUE OF ACETIC ACID.

Excess per cent. of Acetic Acid in the Beer.	Corresponding Degrees of Spirit Indication.									
	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·0	...	·02	·04	·06	·07	·08	·09	·11	·12	·13
·1	·14	·15	·17	·18	·19	·21	·22	·23	·24	·26
·2	·27	·28	·29	·31	·32	·33	·34	·35	·37	·38
·3	·39	·40	·42	·43	·44	·46	·47	·48	·49	·51
·4	·52	·53	·55	·56	·57	·59	·60	·61	·62	·64
·5	·65	·66	·67	·69	·70	·71	·72	·73	·75	·76
·6	·77	·78	·80	·81	·82	·84	·85	·86	·87	·89
·7	·90	·91	·93	·94	·95	·97	·98	·99	1·00	1·02
·8	1·03	1·04	1·05	1·07	1·08	1·09	1·10	1·11	1·13	1·14
·9	1·15	1·16	1·18	1·19	1·21	1·22	1·23	1·25	1·26	1·28
1·0	1·29	1·31	1·33	1·35	1·36	1·37	1·38	1·40	1·41	1·42

From the malt extract the amount of malt used is calculated, 32·0 of malt equalling 21·0 of extract; or, instead of referring to the malt extract tables, 1000 may be subtracted from the original gravity, and the remainder multiplied by ·0028, which will equal the total amount of malt extract per gallon in pounds weight.

EXAMPLES.

(1.) An ordinary Mild Ale.

		1000·0
Specific gravity of alcoholic distillate	=	993·6
Spirit indication,		6·4

This spirit indication, on reference to Table XLI., equals 26·0

Gravity of boiled beer,	=	1·014·2
Add,		26·0
Original gravity,		1·040·2

Now, in reference to Table XL., 1·0402 correspond to 9·950 parts of extract in 100, or ·9950 lbs. per gallon.

Or, if from the original gravity,	1·0402
Be subtracted,	1·000
And the number obtained	402
Be multiplied by	·0025
The product equals	1·005

which does not materially differ from the amount obtained from the tables.

(2.) A beer, by the evaporation process, indicated 8·5 per cent. of alcohol. On reference to the specific gravity table (Table XXXIII.), p. 371, the specific gravity corresponding to this strength is ·9896.

		1000·0
		989·6
Spirit indication,	=	10·4

This, according to Table XLII., corresponds to 47·1;

The gravity of the boiled beer was	1016·2
Add	47·1
Original gravity	1063·3

corresponding, according to Table XL., to 1·5441 lbs. of malt

extract to the gallon. The amount of malt used in the two examples is found thus—

$$(1.)\ \frac{\cdot 9950 \times 320}{210} = 1\cdot 516 \text{ lbs. of malt to the gallon.}$$

$$(2.)\ \frac{1\cdot 5441 \times 320}{210} = 2\cdot 3526 \text{ lbs. of malt to the gallon.}$$

If the beer should have a somewhat large proportion of acetic acid (as in old and hard beers), it will be necessary to take into account the loss of gravity by acetic acid. This complicates the calculation, and is only occasionally required.

The loss of gravity by acetic acid is obtained by the use of Table XLIII. Let us suppose ·36 per cent. of acetic acid to have been found in Example 1; from this subtract ·10 per cent., the amount which may be taken as incidental to healthy fermentation, and allowed for in the table. Thus,

Total acetic acid present, ...	·36
Deduct	·10
Acetic acid to be taken account of, . . .	·26

This ·26, according to the table, equals ·34, the number to be added to the spirit indication.

Spirit indication from alcohol, ...	6·4
,, ,, from acetic acid, ...	·34
Total spirit indication, . . .	6·74

The rest of the calculation is as before.

It may be desirable to examine the malt extract further, and specially with a view to ascertaining whether grape sugar has been used in place of malt or not. This may be done, according to Haarstick, by taking advantage of the fact that most, perhaps all, of the grape sugars of commerce contain Béchamp's amylin, a substance of great rotatory power, and one, moreover, not destroyed by fermentation.

The samples of beer were examined by Haarstick as follows:—·1 litre of beer was evaporated to a syrup, to which alcohol of 90 per cent. was added, drop by drop, from a burette with constant agitation, until a volume of about 300 cc. had been used. The separation of dextrine was completed with 95 per cent. alcohol, until the filtrate did not show the least turbidity when mixed with an equal bulk of 95 per cent. alcohol. The mixture

was then left at rest for twelve hours, filtered, and the greater part of the alcohol distilled off. The remainder was evaporated to dryness on a water-bath, the solid portion dissolved in distilled water, and the solution diluted to a litre, and fermented with yeast at 20°, until all the sugar had been destroyed. The fermentation was completed on the fourth day, and the result of the process was, that beers prepared without grape sugar gave a solution of no rotatory power, while those prepared with grape sugar turned the plane of polarisation 2°·0 to 3°·4 to the right, as observed in Hoppe's scale.

(5.) *The Hop Resin and Glycerine.*—Griessmayer* estimates the hop resin and glycerine by concentrating the beer to one-third of its bulk, and shaking it up with petroleum ether; this, on separation and evaporation, leaves the hop resin. The liquid, now freed from hop constituents, is made alkaline by baryta water, or, better, by barium alcoholate, and shaken up several times with a mixture of two parts of alcohol and three of ether; the latter, on being separated and evaporated in the usual way, leaves the glycerine.

Clausnizer† gives, as the result of his elaborate experiments on the various processes for the estimation of glycerine, the following method, which would appear to be the best hitherto published: 50 cc. of beer are warmed on the water bath to get rid of CO_2, and then mixed with 3 grms. of hydrate of lime and evaporated to a syrup; 10 grms. of powdered marble are then added, the mass frequently stirred, and the whole dried on the water-bath. The dish with its contents is now weighed, and an aliquot part (about two-fifths to three-quarters) put in the extraction apparatus figured at p. 68, and exhausted with 20 cc. of alcohol of 80 to 90 per cent. The alcoholic extract (now about 15 cc.) is mixed with 25 cc. of anhydrous ether, the precipitate separated, and the ether-alcohol received into a weighed flask, the precipitate also being washed with alcohol-ether [2 : 3.] The almost colourless filtrate is freed from alcohol and ether by very slow evaporation. Lastly the glycerine is dried at 100° until in two hours no more than 2 mgrms. are lost. This process will take from two to four hours for normal beer, from four to six for beer to which glycerine has been added. It may be well to burn up the glycerine and subtract the ash found. Clausnizer gives the percentage of glycerine in common German beers as follows:—

* *Deut. Chem. Ges. Ber.*, xi. 292, 293.

† Clausnizer F.: Zur Glycerine Bestimmung in Bier. *Zeitschrift für Analytische Chem.*, xx. 80.

	Alcohol.	Extract.	Glycerine.
Wagening's Bockbier, . .	3·1	6·4	·208
" Beer, ...	3·0	5·2	·206
Rhine beer, ...	2·8	3·9	·237
Bavarian beer, . . .	4·4	6·0	·220
" "	3·7	4·5	·264

(6.) *The Nature of the Bitter used.*—This is the most difficult part of the investigation, and requires a very considerable amount of practical knowledge. Occasionally, if the beer is put in the tube figured at p. 397, small fragments of quassia, calumba, and similar substances will be observed to sink to the bottom as a sediment, and may be detected microscopically; indeed, it is probable that were it possible to obtain the sediment from the beer casks, many foreign matters might in this way be detected.

In most cases it is sufficient to use some of the special processes hereafter described, and restrict the inquiry to proving the absence of picric acid, of picrotoxin, and of any other specially noxious substance which may be suspected. Should, however, the analyst desire to examine the beer generally for various organic principles, the elaborate process as worked out by Dragendorff and others, fully described in the Second Volume of this work, must be used. About 600 to 1000 cc. of the beer are evaporated to a syrupy consistence, and sufficient strong alcohol is added to precipitate the dextrine. The whole is filtered, and after standing some hours, the filtrate, acidulated with sulphuric acid, and shaken up successively with petroleum ether, benzine, chloroform, and (if salicin be sought) amylic alcohol.

Or the beer may be precipitated with acetate of lead, filtered, the excess of lead thrown out by sulphuric acid, and treated with the solvents as described. If inquiry be made as to the nature of the residue left by these different solvents in beer simply made from hops and malt, it appears that—

(1.) The *petroleum ether* extracts—

(*a.*) An amorphous, slightly bitter substance, soluble in ether and alcohol, and partially soluble in water; this is derived from both hops and malt;

(*b.*) A substance precipitable by basic acetate of lead; and one

(*c.*) Becoming red by Fröhde's reagent; both derived from the hop.

(*d.*) A substance derived from the hop alone, becoming red with sulphuric acid and sugar.

(2.) *Benzine* extracts the same substances, and in addition—

(*e.*) A substance derived from the hop, which precipitates tannin;

(*f.*) A substance derived from the malt, becoming dark-brown on the addition of sulphuric acid.

(3.) *Chloroform* extracts (*a.*), (*b.*), and (*e.*), and also (*f.*), a substance partly precipitated by potassium iodide and phosphomolybdic acid;

(*g.*) A substance reducing ammoniacal solution of silver nitrate;

(*h.*) A substance crystallisable from ether. All of these are derived from the malt.

The normal reactions of the substances being known, the following scheme will be found useful, always bearing in mind that few chemists, should they obtain any of the reactions mentioned, would conclude from this alone that the substance is actually present. The reaction would be considered as an *indication only, to be supplemented by other evidence.* Unless this is remembered and acted upon, the most unfortunate errors may be committed by the inexperienced. The beer is most conveniently shaken up with the solvent in the tube figured p. 69; the ether and benzine will float at the top, the chloroform will gravitate to the bottom; in either case separation is tolerably easy. It will, however, be found a good plan, in the first place, to separate the liquids rather roughly—*i.e.*, to draw off the ether, benzine, and chloroform layers, with some of the adjacent liquid, to wash this in the same tube with water, to withdraw the solvent from the water as completely as possible by the separating tube; and if this (as sometimes happens) is not very feasible, to evaporate the impure liquid to dryness in a water-bath, and exhaust the residue with the original solvent. The latter may be, in the first place, concentrated over hot water, and then portions distributed between two or three watch-glasses, and evaporated to dryness.

I. THE ACID SOLUTION.

Petroleum Residue.

(*a.*) It is amorphous, colours sulphuric acid first brown, then violet, and finally red violet. *Traces of Absynthin.*

(*b.*) It is amorphous, colourless, having a hot taste, reddening the skin, and colouring sulphuric acid brownish-red. *Traces of Capsicin.*

(*c.*) It is amorphous, green, is coloured by sulphuric acid and sugar, and gives no precipitate with ammoniacal silver solution. *Resin of the Juniper berries.*

(*d.*) It is crystalline, yellow, and becomes blood-red on warming with cyanide of potash. *Picric acid.*

Benzine Residue.

A. Crystalline residue.

It is not bitter; caustic potash colours it purple-red, sulphuric acid first red, then orange. *Aloetin.*

B. Amorphous residue.

a. The residue soluble in water; does not trouble or reduce gold chloride solution in the cold.

(*a.*) Tannin does not precipitate the solution in water; residue sharp tasting.

1. Sulphuric acid colours it red brown. *Capsicin.*
2. Sulphuric acid colours it brown. *Daphne bitter.*

(*b.*) Tannin precipitates the solution in water; the residue somewhat bitter.

I. Basic lead acetate causes a weak turbidity, sulphuric acid and sugar scarcely redden.

1. Iron chloride colours the watery solution, on warming, brownish-green; taste slightly bitter. *Gentian bitter.*
2. Iron chloride colours the watery solution brown; taste peculiar, almost unsupportably bitter. *Quassiin.*

II. Basic lead acetate strongly precipitates, sulphuric acid and sugar colour it gradually a beautiful cherry-red; taste bitterish. *Cnicin.*

b. The residue soluble in water; does not trouble solution of gold chloride in the cold, but reduces it on warming.

(*a.*) Tannin causes a faint turbidity in the watery solution, ammoniacal silver solution is not reduced. Heated with diluted sulphuric acid, an ericinol smell is developed. Fröhde's reagent colours it black-brown, sulphuric acid and sugar a beautiful red. *Ledum bitter.*

(*b.*) Tannin precipitates the watery solution; ammoniacal solution of silver is reduced. Heated with diluted sulphuric acid, a weak smell of menyanthol is developed. *Trifolium bitter.*

c. The residue soluble in water, precipitates in the cold chloride of gold, but does not reduce it upon warming. Heated with diluted sulphuric acid (1 of acid to 5 of water), it gives a weak benzoic acid smell. *Centaurea bitter.*

d. The residue soluble in water, precipitates in the cold chloride of gold, which it reduces upon warming. Sulphuric acid dissolves it first brown, then gradually violet; after the addition of water

quickly a beautiful violet. Hydrochloric acid of 1·135 specific gravity colours it first green, then a beautiful blue. *Absynthin.*

Chloroform Residue.

A. Chloride of gold does not precipitate, and is not reduced.

a. Tannin gives no precipitate; the residue has a pungent taste. Sulphuric acid colours it dark-brown red; it reddens the skin. *Capsicin.*

b. Tannin precipitates.

(*a.*) Basic lead acetate gives a decided precipitate. Heated with diluted sulphuric acid it is first troubled, then it becomes brown-red, and develops a weak smell of benzoic acid. *Cnicin.*

(*b.*) Basic acetate of lead gives little or no precipitate.

I. *Sulphuric acid colours brown.*

1. Residue bitter.

aa. Strongly bitter. *Quassiin.*

bb. Residue somewhat bitter. *Gentian bitter.*

2. Residue tasting pungent. *Daphne bitter.*

II. *Sulphuric acid colours but slightly yellow or not at all.* *Colocynth bitter.*

B. Chloride of gold does not precipitate in the cold, but is reduced in the warm.

a. Tannin does not precipitate.

1. Intoxicates fish, tastes bitter. *Picrotoxin.*

2. Is tasteless or slightly bitter; caustic potash colours it red-brown. *Constituent of Aloes.*

b. Tannin precipitates.

(*a.*) Ammoniacal solution of silver is reduced. Heated with dilute sulphuric acid, as well as with Fröhde's reagent, there is a strong smell of menyanthol. *Menyanthin.*

(*b.*) Ammoniacal solution of silver is not reduced. With concentrated sulphuric acid and sugar, after long standing, a splendid carmine red develops; heated with diluted sulphuric acid, as well as with Fröhde's reagent, an intense ericolin smell is developed. *Ericolin.*

C. Chloride of gold precipitates in the cold, and is not reduced by the application of heat. Nitric acid colours violet. *Colchicine.*

Heated with sulphuric acid, an odour somewhat like trifolium is developed, then the solution becomes red-brown, and the smell similar to benzoic acid. *Centaurea bitter.*

D. Chloride of gold precipitates in the cold and reduces in

the warm. Sulphuric acid colours brown, then the solution becomes gradually dirty violet. *Wormwood bitter.*

If necessary to go further, search may be made for the alkaloids by rendering the liquid weakly alkaline by carbonate of soda or by ammonia.

II. THE ALKALINE SOLUTION.

I. Residue obtained by shaking up with Benzine.

(1.) It dilates the pupil of a cat.

(*a.*) Platin chloride does not precipitate the aqueous solution. A solution in sulphuric acid gives on warming a peculiar smell. *Atropine.*

(*b.*) Platin chloride precipitates. *Hyoscyamin.*

(2.) It does not dilate the pupil.

(*a.*) The sulphuric acid solution gives with oxide of cerium or bichromate of potash a blue colour. *Strychnine.*

(*b.*) The sulphuric acid solution gives a red colour with nitric acid solution. *Brucin.*

II. Residue obtained from shaking it up with Amylic Alcohol.—(This need only be done if salicin be suspected.) On warming with sulphuric acid and bichromate of potash, a smell of salicylic acid is developed. *Salicin.*

§ 270. A very good process, only aiming at the identification of a few principles, is recommended by Enders; it is as follows:—

The beer is evaporated to a syrup, the dextrine separated by mixing it with three or four times its volume of alcohol, the liquid filtered, and the sugar precipitated by ether. The filtered ether-alcohol solution is evaporated, the residue dissolved in alcohol, mixed with water, and precipitated by means of acetate of lead. The precipitate is filtered, the filtrate put on one side. The washed precipitate is then separated from lead by SH_2, the lead sulphide filtered and washed with alcohol, and the filtrate (as well as the alcohol washing of lead sulphide) evaporated together. The residue is dissolved in chloroform, and the solution warmed with water until all the chloroform is driven off. The *hop bitter*, which remains insoluble, is filtered off, and the filtrate evaporated to dryness. The lupulin in it should taste bitter and have an acid reaction; it is soluble in alcohol, ether, and chloroform; is not precipitated when in solution in weak

spirit by tannic acid, but is precipitated by acetate of lead. Ammoniacal solution of silver is not reduced by it. The filtrate of the first lead precipitate is freed from lead by SH_2, the lead sulphide filtered off and washed with hot water, the excess of SH_2 driven off by warming, and then tannin added to the filtrate. If no precipitate occurs, absynthin, quassiin, and menyanthin are absent. Any precipitate is filtered, dried with carbonate of lead, boiled with alcohol, evaporated, and, lastly, treated with ether. The latter agent dissolves absynthin, which is also soluble in alcohol, and in much hot water; from the latter solution it is precipitated by tannic acid, but not by lead acetate; it is soluble in sulphuric acid, and on careful addition of water to this solution a *violet-blue colour* is produced. Absynthin reduces an ammoniacal solution of silver. Ether leaves menyanthin and quassiin undissolved. Both are soluble in alcohol, and the latter behaves towards tannic acid and acetate of lead like absynthin. Menyanthin reduces ammoniacal solution of silver; quassiin does not.

Picrotoxin may be specially tested for by some one of the following processes:—

Herapath's Process.—Mix the beer with acetate of lead in excess; filter, and transmit sulphuretted hydrogen through the filtrate. Filter again, concentrate the filtrate, and treat it with animal charcoal, which has the property of absorbing the picrotoxin. Wash the animal charcoal, dry at 100°, and boil with alcohol; this dissolves out the picrotoxin, from which it may be obtained in tufts of crystals.

Depaire's Process.—Mix with 1 litre of beer finely powdered rock salt (which throws down the resinous and extractive matters), and shake the liquid with ether; an impure picrotoxin crystallises on separating the ether and evaporating it: or the beer may be simply acidulated with hydrochloric acid and agitated with ether, the ether separated and evaporated as before.

Schmidt's Process.—1. Evaporate the beer in a water-bath to a syrupy consistence, mix it with tepid water till it is perfectly liquid, so as to bring the volume to a third of the liquid used; heat and shake with animal charcoal. Let it stand several hours, filter, and heat slightly; precipitate by basic acetate of lead, and again filter. The liquid should now be of a yellow wine-colour; if not, re-filter through animal charcoal. Add from 5 to 10 cubic centimetres of amylic alcohol, and shake briskly several times at intervals; after twenty-four hours the amylic alcohol, containing the greater part of the picrotoxin, collects on the surface. The remainder is subsequently eliminated by fresh treatment with amylic alcohol. Collect the limpid layers of this alcohol, and

leave the rest to evaporate spontaneously. On the sides of the capsule a yellowish ring forms, and this contains the picrotoxin mixed with resinous substances.

2. *Isolation of the Picrotoxin.*—First, dissolve the resinous product in weak alcohol, evaporate to dryness, recover by a little boiling water containing a small quantity of H_2SO_4, boil to expel any volatile matter, add a little animal black to eliminate all extractive and resinous matter, and, lastly, filter. Evaporate inodorous liquid, and when a fresh bitter taste is developed, shake up with ether; this redissolves the picrotoxin, and collects into a distinct layer on the surface of the liquid. Treat again with ether, and the whole of the picrotoxin is eliminated; finally, the ethereal liquids are mixed, a little alcohol is added, and the whole is evaporated. The white or yellowish ring formed consists of picrotoxin, which then has only to be dissolved in alcohol to furnish the immediate principle in the form of well-defined crystals. These crystals, however, will not be obtained unless the solution be quite free from resinous substances; if not free, and if, for instance, the ethereal solution is of a yellow colour, it must be recovered with water and treated by charcoal, as above described.

Schmidt was able to separate by this process 0·04 grain of picrotoxin in a bottle of beer which had been adulterated with eight grains of Indian berry.*

Dragendorff has modified the method of Schmidt, by adding an excess of acetate of lead, precipitating this by SH_2, and with the lead sulphide getting rid of some colouring matter. The sulphide of lead may be washed and dried, and then boiled with ether, to recover any picrotoxin which has gone down with it.

By the following process the animal charcoal may be dispensed with altogether:—The beer is first evaporated to a syrup, then 4 to 5 vols. of alcohol of 90 to 94 per cent. are added. After maceration for twenty-four hours at a low temperature, the alcoholic extract is evaporated, the residue acidified with diluted SO_4H_2, and treated several times with amyl alcohol or chloroform; but previously to this the fluid should be shaken up several times with benzine, which does not remove any picrotoxin. The rest of the process is similar to that of Schmidt.

§ 271. *Special Tests for Picric Acid.*—If picric acid alone should be sought for, the quickest way is to agitate the beer in the separating tube, described p. 69, with half its volume of amylic alcohol. On separating and evaporating the alcohol, if picric

* M. Schmidt: *Chem. News,* March 12, 1864, p. 122.

acid be present a yellow residue will be left, and can be identified by the action of potassic cyanide, as described below. It will not be worth while testing specially for picric acid, if the beer, on being treated with subacetate of lead, loses nearly all its bitter taste; but if, on the contrary, it continues bitter, picric acid, or some other bitter not precipitable by acetate of lead, is present.

Another test frequently proposed for picric acid is to soak some pure wool in the beer, first gently warmed over the water-bath and acidulated with HCl, when the picric acid will stain the wool yellow. The wool thus stained may next be warmed with aqueous ammonia, the liquid filtered, concentrated to a small bulk, and a few drops of a solution of potassic cyanide added, when, if picric acid be present, a red colour (potassium isopurpurate) will be produced. Picric acid may be also recognised, if present, by spectroscopic examination: the dried extract is exhausted either by amyl alcohol or ether, and the solution examined, comparing any spectrum obtained with that given by a solution of the acid.

The best method, according to W. Fleck, of detecting picric acid in beer, is to evaporate down, say half a litre of the beer to a syrup, mix the residue with ten times its volume of absolute alcohol, filter, wash, evaporate the alcoholic solution to dryness, treat this dry extract with water as long as the water is coloured, evaporate down the watery extract to dryness, and extract with ether. The ether will contain any picric acid in a state pure enough to weigh, if not absolutely pure. The ether may be driven off and the picric acid taken up by chloroform or benzole, and crystallised out from either of those solvents.*

§ 272. Mr. Sorby has endeavoured to discover by spectral analysis differences between picric acid, gentian, calumba, and chiretta. The characters of the pure colouring-matters of malt and hops, when single and unfermented, have been already described. They are, however, modified somewhat by fermentation and by keeping in the cask, and the following is a description of what may be found in pure beers. The colouring-matter is first separated by evaporating down and precipitating by alcohol; the alcoholic filtrate is in turn evaporated, and the residue dissolved in water. On now adding to this aqueous solution sodic hypochlorite, it becomes gradually flesh-coloured, and if it is strong a spectrum can be obtained. This spectrum is lightly shaded to C $\frac{2}{3}$ D, then dark to D $\frac{1}{2}$ E, afterwards very dark; and when most advantageously seen half dark from D $\frac{2}{3}$ E to F, then easily shaded to F $\frac{1}{2}$ G, farther on very dark; and there is a broad absorption-

* H. Fleck, *Correspondenz-Bl. d. Vereins. Anal. Chem.*, iii. 77.

band from E$\frac{1}{2}b$. If more hypochlorite is added, it becomes deeper orange, and finally orange yellow. No difference could be discovered spectroscopically between gentian, chiretta, and hops. Calumba root it is possible to detect as follows :—

A sample of pure and one of suspected beer are evaporated down. [A beer may be suspected if the extract is bright yellow.] Two observation tubes are taken, and the pure beer diluted until it gives a spectrum easily shaded from D$\frac{1}{2}$E to E$\frac{1}{2}b$, then moderately dark from $b\frac{3}{5}$F, afterwards dark. In the other tube is placed as much of the suspected sample as will give a colour of about equal intensity, and in both cases about one-fourth of the mixture must be alcohol, in order to avoid a precipitate. Sodic hypochlorite is now added to both slowly, and in about equal proportion; when pure, beer will become first red, and then flesh-coloured, with a spectrum moderately dark from $b\frac{3}{5}$F to F$\frac{1}{7}g$, then half dark to F$\frac{1}{2}g$, afterwards dark; whilst beer containing calumba root is coloured orange-red, and gives a spectrum lightly shaded from D to D$\frac{1}{2}$E, afterwards half dark from D$\frac{2}{3}$E, then dark. Too large an amount of hypochlorite must not be added, or the colour is then too like that of pure beer. Picric acid, when in beer, gives a spectrum which is easily shaded from F$\frac{1}{2}g$ to F$\frac{3}{4}g$, then half dark to about g, afterwards very dark. On addition of sulphuric acid the spectrum is lightly shaded from F$\frac{1}{2}g$ to F$\frac{3}{4}g$, then half dark to beyond g; afterwards very dark.

Salicylic Acid is used occasionally in brewing. If the beer, concentrated to a small bulk, is acidified with hydrochloric acid and shaken up with ether, the latter solvent will extract the organic acid, and it may be identified by the colour it gives with ferric chloride, and by its physical properties.

§ 273. (7.) *The Ash.*—The analysis of the ash of beer differs in no degree from an analysis of ash in general, and is carried out in the principles detailed, p. 97 *et seq.* The substances to which the analyst's attention is specially directed are—the amount of salt, the presence or absence of iron (often added in the form of sulphate to porter), alum, and lead.* Of these the only one necessary to allude to further is the salt.

The salt in beer is determined with sufficient accuracy by charring in a platinum dish the extract from 70 cc. of beer (it is not well to burn to a complete ash, for in doing so there is always a considerable loss of chlorides). The charred mass is boiled up with successive portions of distilled water, filtered, and the

* Many firms now use large copper coolers, but no injurious amount of copper appears to have been as yet detected in beers.

filtrate made up to a known bulk, from which a convenient fractional portion is taken, and titrated with a solution of nitrate of silver (4·79 grms. to the litre), 1 cc. = 1 mgrm. of chlorine, using as an indicator neutral chromate of potash. The chlorine found is calculated and expressed as common salt, every mgrm. of salt, when 70 cc. are taken, being equivalent to 1 grain in the gallon. Mr. Griffin's convenient measure, the septem or one-hundredth of a gallon, may, of course, be used, and grains instead of grammes—each grain measure of nitrate of silver being made to correspond to one-tenth of a grain of common salt per gallon. Should the amount thus found indicate more than 50 or 60 grains per gallon, a second determination of chlorine should be made by the more accurate gravimetric method of weighing the chlorine as chloride of silver. It may even be advisable to make a qualitative and quantitative examination of the soluble portion of the ash; for, if called as a witness, the analyst must be prepared to state positively the amount of chloride of *sodium;* nor can he well do this simply from the soluble chlorine, for that may represent other chlorides besides chlorides of sodium.

The amount of salt derived from the hops and malt can approximately be determined, as Mr. Gatehouse has shown,*—First, for the malt: by taking the original gravity, as before described (p. 415), obtaining thence the quantity of malt originally used in the beer, and reckoning the malt to contain ·025 per cent. of salt (and certainly no malt will be found to exceed this). Then, for the hops: the possible maximum of salt in hops is ·345 per cent. The quantity used in brewing being seldom, if ever, more than 20 lbs. per quarter of malt for bitter beer, and generally less than half this amount for strong beer, and this weight of malt giving at least 72 gallons, the salt derived from the hops cannot in bitter beer exceed 6·7 grains, and in strong beer 3·35 grains per gallon.

Thus, to take the first example (p. 423), the original gravity of which was 1·0402, corresponding by the tables to 9·950 lbs. of malt extract per gallon. Since 320 of malt equal 210 of extract, and there are 7000 grains in the pound—

$$\frac{9 \cdot 950 \times 320 \times \cdot 025 \times 7000}{210 \times 100}$$

= 2·65 grains of salt per gallon as the possible maximum from the malt, the beer in question not being a bitter beer. Add to this 3·35 as possible maximum amount of salt from the hops—

* The Amount of Salt in Beer. *Analyst*, No. 20, 1877.

2·65 from malt,
3·35 from hops,

6·00 salt possible from both malt and hops.

Now, if the composition of the water used in brewing be known, one-third more than the actual quantity of salt in the water present may be added to the number representing the salt from the hops and malt, and the data are then complete for the analyst to form his judgment. The amount of salt in the water used will, however, only occasionally be known.

The numbers used in the above calculations being constants, the process is shortened by simply deducting 1000 from the original gravity, and multiplying by ·066, the result giving the salt in grains per gallon. Thus, taking an example from Mr. Gatehouse's excellent paper :*—

		Per cent.
Beer found to contain alcohol, ...		5·2
Malt extract, ...		7·38
Specific gravity of alcohol equals ·9911; the spirit indication therefore equals 8·9, giving an original gravity, ...		38·6
Gravity of boiled beer, ...		1030·6
Original gravity of wort, ...		1069·2
Salt due to malt alone, ...	69·2 × ·066 =	4·567
Salt due to hops, ...		3·350
Salt due to water, unknown.		
Possible total due to malt and hops, ...		7·917

The amount of salt actually found being 8·55

It has been suggested that the concrete sugar† so largely and legitimately used by brewers, sometimes contains a considerable amount of chlorides. If samples are found, occasionally, with more than a trace of chloride, it is because the sugar itself has been prepared for the brewers; nor can there be any difference

* *Op. cit.*

† It is possible for arsenic to be found in beers manufactured from glucose, for in certain kinds of the latter arsenic is occasionally discovered, the substance probably having been introduced by the use of an arsenical sulphuric acid in the process of manufacture. The darker in colour the glucose, the more likely is it to be arsenical; thus, M. Ritter found—

	Grm.
In White Glucose,	0·0105 arsenic per kilogramme.
,, Yellow ,,	0·0170 ,, ,,
,, Black ,,	0·1094 ,, ,,

Clouet, in the examination of a very large number of arsenical glucoses, found as a minimum 0·0025 grm., as a maximum 0·0070 grm., and as a mean 0·0051 grm. metallic arsenic per kilogramme. (T. Clouet, Du glucose arsenical. *Ann. d'Hygiène Publique*, xlix., Jan., 1878.)

whether the brewer adds the salt as salt, or first mixes it with sugar. However, analytical proof of sufficient chlorides *naturally* present in concrete sugar, to raise the salt in beer made from ordinary materials to over 50 grains per gallon, is wanting; and all the evidence in its favour has been derived from loose statements.

BIBLIOGRAPHY.

Analytic Report on Dublin XXX Porter. *Med. Press and Circuar*, 1869.

BABRUEL.—Analyse d'une bière qu'on croyait falsifiée. *Ann. d'Hyg. et de Méd. Lég.*, 1833, t. x., p. 74.

BALLEY.—"Handbuch der Technischen Untersuchungen." Leipzig, 1874.

BLAS.—Recherche de la picrotoxine dans la bière. *Bull. Acad. de Méd. de Belgique*, 1869, p. 1232. De la présence de l'Acide Salicylique dans les bières. Paris, 1879.

BONNEWIN.—Note sur la picrotoxine. *Bull. Acad. de Méd. de Belgique*, 1869, p. 837.

BRUNAER.—Présence de l'acide picrique dans la bière. *Journ. Pharm. et Chim.*, 2e série, 1873, t. xviij., p. 247.

CLAUSNIZER, F.—"Zur Glycerine Bestimmung in Bier." *Z. für Anal. Chemie*, xx. 80.

DRAGENDORFF.—"Recherche des substances amères dans la bière." Paris, 1876.

ENDERS.—*Arch. f. Pharm.*, Bd. 185, p. 225.

GATEHOUSE, J. W.—The Amount of Salt in Beer. *Analyst*, No. 20, 1877.

HAARSTICK.—*Chem. Centrbl.*, 1876; also *Journ. Chem. Soc.*, ii., 1877, p. 372.

HASSALL, A.—"Food: its Adulterations detected." London, 1876.

LASSAIGNE, J. L.—Note sur le moyen de constater et de démontrer la présence de l'acide picrique introduit dans la bière. *Journ. Chim. Méd.*, 3e série, 1863, t. ix., p. 495.

LINTNER, C.—"Lehrbuch der Bierbrauerie," 1877.

MEUREM, V.—Recherches chimiques sur les bières plombiféres. *Journ. Chim. Méd.*, 3e série, 1863, t. ix., p. 595.

MULDER.—Des falsifications de la bière. *Ann. d'Hyg. et de Méd. Lég.*, 2e série, 1861, t. xvj., pp. 33, 430.

PASTEUR, M. L.—"Etudes sur la bière, ses malades, causes qui les provoquent," &c. Paris, 1876.

POEL.—Moyen de déceler l'acide picrique dans la bière. *Journ. Pharm. et Chim.*, 3e série, 1856, t. xxix., p. 465.

RAUWEZ, J. V.—Moyen simple de reconnaître une bière à l'aloes. *Journ. Chim. Méd.*, 4e série, 1862, t. x., p. 233.

SCHMIDT.—Bière falsifiée avec de la picrotoxine. *Journ. Pharm. et Chim.*, 3e série, 1863, t. xliii., p. 170.

SCHÜTZENBERGER, P.—"On Fermentation." London, 1876.

SCHULZE.—Maltose. *Deut. Chem. Ges. Ber.*, vij. 1047-1049.

SOUBEIRAN.—"Dictionnaire des falsifications." Paris, 1874.

STIERLIN, R.—Das Bier und seine Verfälschungen, Bern, 1878.

SULLIVAN, C. O.—Maltose. *Journ. Chem. Soc.*, i., 1876, p. 478.

VINCENT.—"Dictionary of Arts and Manufactures," Art. Beer.

VOGEL, HERM. W.—"Practische Spectral Analyse," &c. Nordlingen, 1877.

WANKLYN in "Manual of Public Health," ed. by Ernest Hart.

WATTS.—"Chemical Dictionary."

WENKE.—"Das Bier und seine Verfälschung." Weimar, 1861.
WITTSTEIN, G. C.—Detection of Adulterations in Beer. *Arch. Pharm.* [3], v. 25-23.

WINE.

§ 274. *Constituents of Wine.*—Wine is the fermented juice of the grape, with such additions only as are essential to the stability, or keeping of the liquid (*Dupré*). The constituents of grape juice and wine may be arranged and compared as follows (*Neubauer*) :-

MUST.	WINE.
Water.	Water.
Grape sugar.	Grape sugar (0 to several per cents.)
	Alcohol.
Albuminoid bodies.	Residues of albuminoid bodies.
	Acetic acid.
	Succinic acid.
Hydro-potassic tartrate.	
Tartrate of lime.	Tartrate of lime, Tartaric acid, } In smaller proportions than in "Must."
Vegetable mucus.	
Gum.	Gum.
Malic acid (in bad seasons).	Malic acid (in bad seasons).
Salts of ammonia and of similar bases.	
Small mixtures of colouring-matters.	Colouring-matters.
	Glycerine.
Organic acids in combination and certain extractive matters.	Organic matters in combination and certain extractive matters.
	Caproic ether, Caprylic ether, } So-called œnanthic ether.
	Unknown odorous ethers.
	Tannin.
Mineral matters.*	Mineral matters.
	A few ferment cells and similar forms.

* The mineral matters of the ash of eighteen samples of grape juice have been quantitatively determined by Mr. Carter Bell, Analyst (November, 1881); the chief results are as follows :—

	Potash.	Soda.	Chlorine.	Sulphuric Acid.	Phosphoric Acid.	Lime.	Magnesia.	Iron Phosphate.	Alumina Phosphate.	Lime. Phosphate.	Silica.
Maximum, .	54·24	10·54	3·39	13·68	7·28	13·99	12·57	1·68	3·85	23·73	·98
Minimum, .	31·23	·29	·29	3·14	·22	·65	·96	·05	·05	3·13	·08
Mean, . .	42·14	3·37	1·09	9·14	3·00	4·55	9·67	·63	·87	12·78	·29

may be compared with the mineral constituents of wine given at

§ 275. *Changes taking place in Wine through Age.*—Berthelot * has made several analyses of wines 100 and 45 years old respectively, which are interesting as contributing to more accurate knowledge regarding the effect of age upon wine. The wines were both samples of Port. The one 100 years old had a large deposit of colouring-matter, and was yellow; the colour of the second sample was dark, but yet lighter than that of new wine. The results of the analyses are as follows:—

	Port wine, 100 years old.	Port wine, 45 years old.
Specific gravity,	·988	·991
Total residue at 100°,	3·36	5·30
Sugars, reducing,	1·25	3·15
Sugars, after the action of dilute acid,	1·29	3·68
Acid, calculated as tartaric acid,	5·17	5·46
Tartaric ether,	1·11	1·17
Cream of tartar,	·27	·42
Glycerine,	15·0	16·1

The analyses of the deposits gave the following results:—

	Wine 100 years old.	Wine 45 years old.
Sugar, reducing,	1·25	3·15
Cane-sugar,	·04	·53
Pure acids,	·51	·52
Acids as ethers,	·27	·28
Cream of tartar,	·03	·04
	2·10	4·52
Glycerine,	1·16	·98

It would then seem that there is a gradual deposit of the colouring-matter, and that some of the sugar has disappeared from the old wine, which gives a smaller residue. Cane-sugar is practically absent in the sample 100 years old, a fact which Berthelot interprets as confirmatory of his observation of the slow invertive action of organic acids on cane-sugar. From the quantities of tartaric acid existing as ethers, and the same amount of acids in new wine, it would appear that the wine loses about a quarter of its acidity by etherification. The experiments of Macagno may also be here cited, from which it appears that in wines of the same class the tannin decreases through age, while the glycerine increases.

The Table† on pp. 440, 441 gives examples of the quantities found of the chief ingredients of wine.

* *Comptes Rendus*, 88, 1879, 626.

† Drawn up by Dr. Dupré. *Proceedings of Society of Public Analysts*, i., 1876, p. 77.

TABLE XLIV.—WEIGHT IN GRAMMES OF SOME OF THE CHIEF
UNDERMENTIONED

Particulars of Wines Analysed.	Doz.	Vintage.	Specific Gravity.	Absolute Alcohol.	Free Fixed Acid as Tartaric Acid.	Free Volatile Acid as Acetic Acid.	Total Free Acid as Tartaric Acid.	Real Tartaric Acid.
Hock, white,	30s.	1862	993·43	95·6	3·48	0·57	4·20	...
,, ,,	40s.	1859	993·48	92·0	4·20	1·14	5·62	2·550
,, ,,	120s.	1857	992·81	104·4	4·31	0·93	5·37	0·675
Claret, .	15s.	1865	995·58	85·3	4·24	1·47	6·08	0·675
,, .	48s.	1865	995·03	120·0	4·24	1·74	6·41	1·875
,, .	66s.	1861	994·73	85·3	3·23	1·80	5·48	1·838
Hungarian, red,	21s.	...	992·07	113·6	3·56	2·49	6·68	0·600
,, white,	34s.	...	992·88	95·4	5·33	1·47	7·16	0·675
,, ,,	42s.	...	993·09	94·9	4·74	1·80	6·99	0·375
Greek wine, ,,	20s.	...	994·56	107·2	3·41	3·00	7·16	0·675
,, ,, ,,	28s.	...	992·25	124·5	4·54	1·68	6·64	...
,, ,, ,,	36s.	...	993·17	138·9	2·33	1·77	4·54	0·300
Sherry, .	22s.	1865	994·09	172·0	2·70	1·53	4·61	0·187
,,	high price,	1860	997·93	178·1	3·08	1·68	5·18	0·262
,,	,, ,,	1857	998·30	184·0	2·81	1·62	4·84	0·150
Madeira, E.I.,	60s.	...	993·94	177·5	3·26	1·68	5·36	0·300
,,	high price,	1812	994·15	180·0	4·20	3·27	8·25	...
Port, .	32s.	1864	1004·76	185·6	3·08	0·84	4·13	0·225
,,	high price,	1854	997·42	175·3	3·54	1·07	4·88	0·225
,,	,, ,,	1842	986·95	182·6	2·66	1·08	4·01	0·150
Marsala, .	16s.	old	996·65	167·1	1·88	1·11	3·26	...
,, .	20s.	very old	999·65	168·9	2·25	1·38	3·98	0·150

CONSTITUENTS OF 1 LITRE (1000 CC., OR 1000 VOLUMES, OF THE WINES (DUPRÉ).

Total Dry Residue.	Grape and Fruit Sugar.	Total amount of Ash.	Carbonate of Potassium.	Sulphates and Chlorides.	Phosphate and Carbonate of Calcium.	Total amount of Phosphoric Acid.	Alcohol in Fixed Ethers.	Alcohol in Volatile Ethers.	Total Alcohol in Ethers found.	Total Alcohol in Ethers calculated.	Proportion per cent. of Alcohol found to Alcohol calculated.
18·63	...	1·95	0·58	0·76	0·60	0·32	0·132	0·230	0·362	0·360	100·5
18·55	0·12	1·70	0·07	0·78	0·85	0·30	0·199	0·239	0·438	0·458	95·7
20·60	1·12	1·45	0·14	0·46	0·85	0·35	0·225	0·239	0·464	0·493	94·3
21·40	4·31	2·08	0·66	0·95	0·48	0·33	0·155	0·197	0·352	0·476	74·0
24·33	2·04	2·25	0·66	1·05	0·55	0·30	0·186	0·248	0·430	0·581	74·6
18·00	0·95	2·00	0·38	0·99	0·63	0·30	0·166	0·216	0·382	0·429	88·8
20·85	1·47	1·85	0·41	0·91	0·53	0·35	0·151	0·358	0·509	0·656	77·6
18·20	0·61	1·75	0·14	0·81	0·80	0·25	0·186	0·271	0·457	0·613	74·5
18·13	0·24	1·88	0·12	0·90	0·85	0·25	0·162	0·273	0·435	0·596	73·0
25·30	2·00	2·25	0·07	1·18	1 00	0·25	0·224	0·214	0·438	0·690	63·6
24·42	1·12	3·05	0·41	2·01	0·62	0·25	0·384	0·179	0·563	0·707	79·6
25·50	3·64	3·75	0·21	2·49	1·05	0·45	0·245	1·207	0·453	0·530	85·1
42·00	25·65	4·50	0·07	3·63	0·80	0·18	0·206	0·216	0·422	0·639	66·1
53·50	29·70	5·50	0·18	4·41	0·95	0 25	0·290	0·391	0·681	0.749	90·8
56·44	35·10	5·13	0·07	4·18	0·88	0·13	0·262	0·469	0·731	0·722	101·2
43·47	20 80	3·90	0·27	2·52	1·10	0·42	0·305	0·382	0·687	0·774	88·7
45·41	16·29	3·59	0·17	1·93	1·49	0·50	0·460	0·773	1·233	1·207	102·1
75·57	43·31	2·48	0·48	1·34	0·65	0·35	0·302	0·128	0·430	0·620	69·4
53·90	22·84	2·58	0·66	1·37	0·55	0·33	0·351	0·220	0·571	0·697	84·9
31·01	10·10	2·10	0·69	0·86	0·45	0·33	0·283	0·331	0·614	0·595	103·2
49·83	32·40	2·25	0·21	1·54	0·50	0·18	0·256	0·189	0·445	0·447	99·3
57·48	37·60	3·13	0·55	1·92	0·65	0·23	0·333	0·216	0·549	0·550	99·8

§ 276. *Adulterations of Wine.*—The adulterations of wine bought at a fair price from respectable firms do not appear numerous; but, on the other hand, low-priced wines (especially such as are retailed to the poor, and are supplied to workhouses) are often of extremely bad quality, and sometimes entirely fictitious.* Thus Ports are fortified with brandy, coloured by various ingredients,† plastered with gypsum and mixed with inferior wines; salt of tartar and œnanthic ether are often added to give an appearance of age, alum to increase the brilliancy of hue; and occasionally (as an impurity, or as an unintentional adulterant) lead and other metals are detected. Sherries, again, are plastered and fortified to a considerable extent, and Clarets, Madeira, and Champagnes are all subject to somewhat similar sophistications.

§ 277. *Analysis of Wine.*—A complete analysis of wine embraces the following:—

1. Determination of alcohol.
2. Percentage of solid residue.

* Dr. A. Cameron has found in Port wine supplied to Irish workhouses 12 per cent. of solid residue, one-half of which was composed of grape sugar. According to Maumené, the Russian military pharmacopœia contains the following receipt for making a Port wine:—Cider, 3 kilogrms.; kino, ·008 kilogrm.; Old Hock, with cider, 3 kilogrms.; brandy, 1 kilogrm.; nitric ether, alcoholised, ·008.

† *Geropiga.*—The use of geropiga in the manufacture of Port wines engaged much the attention of the Excise, in 1849, and has preserved for us some interesting correspondence. There is extant a letter from Consul Johnstone to Lord Palmerston, in which the Consul, writing from Oporto, states that every pipe of geropiga contains about 35 imperial gallons of brandy; the other ingredients being colouring and sweetening matters, and unfermented grape juice. He also gives it as his opinion, that geropiga was used to give to wines the appearance of possessing qualities which they had not, and of concealing the bad qualities which they had. The absolute alcohol of the geropiga was about 35 per cent., but the qualities and strength varied much. It appears to have been a coarse liqueur made with must, brandy, and elder-berries. From the same correspondence we are enabled to trace the evil influence of the professional "tasters," of whom there were twelve in Oporto, where, agreeably to the law, "the trials of wine lasted seven hours daily." The tasters for about six consecutive hours were busily engaged in tasting promiscuously all sorts of wine—sweet and dry, light, full, strongly alcoholised, or the reverse—each of them trying from 150 to 300 samples in the six hours. It was from the verdicts of these men that the wines were arranged according to their quality. Naturally enough, their jaded palates were quite incapable of appreciating the finer qualities and delicate shades of difference, and it need cause no surprise to find the Consul remarking that "in the Douro this practice occasions extensive sophistications, and leads to the confounding of various wines of that district."

3. Estimation of succinic acid and glycerine.
4. „ volatile and fixed acids.
5. „ ethers.
6. „ sugar.
7. „ albuminous matters and ammonia.
8. „ tannin.
9. Examination of the colouring-matters.
10. Estimation and analysis of ash.

1. *Alcohol.*—Wines, in regard to their alcoholic content, may be divided into two classes—viz., *natural wines*, the strength of which has not been increased by the addition of spirit; and *fortified wines*, such as those of Spain and Portugal, which absolutely *require* the addition of a certain amount of spirit to preserve them. Natural wines contain as a minimum 6 per cent., and as a maximum a little over 12 per cent., of absolute alcohol by weight. The percentage of alcohol in fortified wines depends, of course, entirely on the operator; it appears to range usually from 12 to 22 per cent. by weight. The alcohol is returned as ethylic, but there are always traces of the higher homologous alcohols—*e.g.*, propylic, butylic, and amylic. If the analyst desires to estimate the different proportions of these, a large quantity of wine must be distilled, the distillate redistilled in fractions, and ultimately oxidised into the corresponding acids, the latter being more easily separated than the alcohols. The method of determining the alcohol in wine differs in no essential feature from the processes described at p. 378.

2. *The Solid Residue.*—The dry extract from pure natural wines is from 1·5 to 3 per cent.; the presence of sugar in fortified wines may raise the extract to 6·8 or 10 per cent. The solid residue may be taken by simply evaporating 10 cc. to dryness, which can be done rapidly, without any decomposition of the solids, by using a large flat platinum dish, and thus spreading the 10 cc. out in a thin layer. This method is, however, somewhat inconvenient, and causes a loss of glycerine; therefore, the indirect process for beer, given at p. 415, may be employed instead, wine extract being considered equal in density to malt extract.* But in wines containing much ash (since the

* A. Gautier (*Annales d'Hygiène Publique*, t. xlvii., 118, 1877) has recommended in all cases the evaporation of 5 cc. of wine on a watch-glass, in a vacuum, without the application of artificial heat. This method takes from two to six days, according to the temperature, for completion, so that it is scarcely applicable for technical purposes; but it is evident that a heat of 30°, whilst greatly expediting the process, would in no way impair its accuracy.

mineral constituents of the latter seriously affect specific gravity, containing in a given specific gravity about twice as much substance in solution as a sugar solution of the same gravity), it is necessary to subtract from the percentage of extract thus estimated, the percentage of ash found in the same wine; or if the amount of extract without the ash is required, twice the percentage of ash has to be subtracted from the percentage found. Dupré and Thudichum give the following examples:

RONENTHALER, 1859 (£15 Ohm).

	Per cent.
Specific gravity of de-alcoholised wine, . . .	1008·01
Percentage of extract (see table, p. 416), . .	2·041
Percentage of ash found, ...	0·170
Total solid constituents, ...	3·952
To find total solids minus ash, subtract again .	0·170
Total solid constituents, ...	1·701

SHERRY, 1865.

Specific gravity of de-alcoholised wine, . . .	1017·56
Percentage of extract from specific gravity (see table, p. 416), ...	4·467
Percentage of ash found, ...	0·515
	3·952
Subtract ash, ...	0·515
Total solid constituents, ...	3·437

H. Hager,* after evaporating off the alcohol, and making up the wine to its original volume by means of water, determines the amount of extract from the following table, which is based on his own experiments, and differs a little from the malt extract table p. 416.

The extract and amount of alcohol being known, it is, in certain instances, possible to detect the *watering* of wine, although such a diagnosis can only be made when the analyst is intimately acquainted with the kind of wine under examination, and in some cases with the characters of the particular vintage. The Bordeaux wines, according to Girardin and Pressier, give almost always the same amount of extract, varying only within the imits of 20 to 20·8 grms. the litre; and the proportion of alcohol also is fairly constant—viz., from ·005 to ·015, the mean being ·010 per litre. From these data they calculated the

* *Chem. Centrbl.*, 1878, 415.

TABLE XLV.

Per cent. of Extract.	Specific gravity, 15°·0	Per cent. of Extract.	Specific gravity, 15°·0	Per cent. of Extract.	Specific gravity, 15°·0
0·50	1·0022	5·25	1·0239	10·00	1·0461
0·75	1·0034	5·50	1·0251	10·25	1·0473
1·00	1·0046	5·75	1·0263	10·50	1·0485
1·25	1·0057	6·00	1·0274	10·75	1·0496
1·50	1·0068	6·25	1·0286	11·00	1·0508
1·75	1·0079	6·50	1·0298	11·25	1·0520
2·00	1·0091	6·75	1·0309	11·50	1·0532
2·25	1·0102	7·00	1·0321	11·75	1·0544
2·50	1·0114	7·25	1·0332	12·00	1·0555
2·75	1·0125	7·50	1·0343	12·25	1·0567
3·00	1·0137	7·75	1·0355	12·50	1·0579
3·25	1·0148	8·00	1·0367	12·75	1·0591
3·50	1·0160	8·25	1·0378	13·00	1·0603
3·75	1·0171	8·50	1·0390	13·25	1·0614
4·00	1·0183	8·75	1·0402	13·50	1·0626
4·25	1·0194	9·00	1·0414	13·75	1·0638
4·50	1·0205	9·25	1·0426	14·00	1·0651
4·75	1·0216	9·50	1·0437	14·25	1·0663
5·00	1·0228	9·75	1·0449		

[N.B. The specific gravity increases or diminishes ·00024 for each degree.]

amount of genuine wine present in any samples. Thus, supposing the extract in a Bordeaux wine to be 14·5, then

$$\frac{1000 \times 14{\cdot}5}{20{\cdot}9} = x, \text{ or } 725{\cdot}00$$

i.e., the litre contains 725 cc. of wine, the rest being alcohol and water. To know the quantity of alcohol added, it is necessary to ascertain how much the 72·5 parts of wine contain of absolute alcohol;

$$10 : 10 : : 72{\cdot}50 : x$$
$$x = 7{\cdot}25.$$

If the absolute alcohol is found, for example, to be 0·11, then, subtracting 7·25 from 11, it is supposed that 3·75 of alcohol has been added.

That this process, as applied to the Bordeaux wines, is in the main correct, is supported by the fact that the Rouen wine-merchants have frequently paid duty on the excess of alcohol, &c., which Girardin and Pressier found in their wines.

§ 278. 3. *Estimation of Succinic Acid and Glycerine.*—Half a litre to a litre of wine is decolourised with animal charcoal, filtered, and the charcoal well washed with water; the filtrate and washings are then evaporated down in the water-bath, and the drying finished in a vacuum. The residue, when dry, is treated with a mixture of one part of strong alcohol and $2\frac{1}{2}$ parts of rectified ether. The latter is driven off by floating the dish in warm water, and the whole evaporated again on a water-bath. The residue is now neutralised with lime-water, which combines with the succinic acid, and forms succinate of calcium. The glycerine is dissolved out by alcohol and ether, and weighed either directly or by loss. The succinate of calcium remaining behind is impure, and should be well washed with spirit before weighing. Every 100 parts of calcic succinate equals 75·64 of succinic acid ($H_2C_4H_4O_4$); and since Pasteur has shown that 112·8 parts of grape sugar (107 of cane) yield about 3·6 of glycerine and 0·6 part of succinic acid, it follows that in a natural wine the glycerine would amount to about one-fourteenth part of the alcohol present.

Reichardt recommends the following process:—To 100 cc. of wine (decolourised by animal charcoal, should it be a red wine), 5 grms. of freshly slaked lime are added, and evaporated to dryness. The residue is powdered and exhausted by digestion for a few hours with 30 cc. of absolute alcohol, or 7 cc. ether, and 23 alcohol of 90°. The liquid is filtered and evaporated to dryness under 100° in a tared dish, and the product weighed.

König* combines Pasteur and Reichardt's processes, that is, he recommends the evaporation with burnt lime, and extracts with 100 parts of 90 per cent. alcohol, and 150 parts of ether; evaporates the ether-alcohol off at from 40° to 50°, and weighs.

Stierlin† evaporates the liquid without any addition to one-fifth or one-sixth of its volume, extracts with hot absolute alcohol, and uses this alcoholic extract for the estimation of the sugar, non-volatile acids, bitter matters, alkaloids, and glycerine. For the estimation of the last, a measured portion of the alcoholic extract is freed from alcohol by evaporation, and then evaporated down to dryness with slight excess of caustic lime. The glycerine is extracted with ether alcohol and ether (2:3), or with alcohol and chloroform. (See also the process for extracting glycerine from beer, p. 425.)

Raynaud has pointed out that although the processes in

* König. "Taschenbuch der Nahrungs.-u. Genussmittel-Lehre." Nördlingen, 1878.

† Stierlin. "Das Bier," &c. Bern, 1879.

use for the estimation of glycerine are fairly exact, yet with plastered wines too high results are obtained; for if there is any considerable amount of sulphate of potash, it is decomposed by lime, and hydrate of potash is formed, which is dissolved by glycerine in the presence of alcohol, and is weighed with it. He therefore recommends the following process:—The liquid operated upon is evaporated to about one-fifth of its volume, and the potash precipitated by hydrofluorsilicic acid and filtered. The filtrate is made weakly alkaline by the addition of hydrate of baryta; sand is also added, and the mass is evaporated to dryness in a vacuum; the dry residue is then extracted with a very large volume of absolute alcohol and ether, as much as 300 cc. for 250 cc. of wine being recommended. With the improved processes of extraction which we now possess, however, this is quite unnecessary, and 50 to 100 cc. in a Soxhlet's apparatus (see p. 67) will have quite the same effect as a much larger quantity. On the evaporation of the alcohol and ether, the glycerine is allowed to stand for twenty-four hours in a vacuum over phosphoric anhydride; finally, it is put into a tube, a perfect vacuum formed, and distilled into the cool part of the tube by a temperature of 180°.

Lallien* has proposed the volumetric determination of glycerine by titration with chameleon, but Liebermann† has examined both Griessmayer and Lallien's processes, and they appear to be untrustworthy, for the most part giving results too low. It is evident that a careful determination of the glycerine in a natural wine, and its proportion to the alcohol present, combined with the percentage of dry extract, will greatly help to solve the question as to whether water has, or has not, been added.

§ 279. 4. *Acids in Wine.*—All wines possess an acid reaction, due to acids, which are conveniently divided into *volatile* and *fixed.* The volatile acid of sound wine, according to Pasteur, never exceeds 2 to 3 decigrms. per litre; in wines a little deteriorated much higher values may be found. Dr. Dupré puts the amount of volatile acid, expressed in terms of acetic acid, as 0·3 to 0·6 per cent. by weight in volume. About one-fourth of the total acidity in white natural wines should be due to volatile acids, and in red and fortified wines the volatile should not amount to more than about one-third of the total acidity. The non-volatile acids appear to be chiefly malic and tartaric (sometimes part of the tartaric being replaced by succinic); the former, according to Dupré, predominating in pure natural wines, and largely so in

* *Bull. Soc. Chim.*, xxxiii. 259.

† Liebermann: "Ueber die Methoden von Griessmayer u. von Lallien zur Bestimmung von Glycerin in Bier." *Verhandlungen des Vereins zur Beforderung des Gewerbfleisses*, 1880.

fortified liquors; whilst in plastered wines it is often present to the total exclusion of tartaric acid.

In artificial wines, it is common enough to find a considerable amount of free tartaric acid; but the mere detection of free tartaric acid is not enough to prove adulteration, since this is found in small quantity in many natural wines. If, however, with a small amount of free acid there is a preponderance of tartaric acid, then sophistication may be suspected. It has been suggested that such free acid may be recovered from the wine by agitation with ether, but J. Nessler, in a direct experiment, could only recover 3·93 per cent. of the free tartaric acid present when the wine was directly treated with ether; 25 per cent. when the wine was evaporated to a syrup. He recommends the following processes:—

The wine is agitated with tartar and divided into two parts, to one of which a few drops of concentrated acetate of potassium solution is added, and the mixture carefully observed, noticing whether any tartar crystals form. Errors are avoided by comparing the one portion to which a few drops of the potassium acetate has been added, with the other portion to which no acetate has been added, the separation of the tartar crystals being a proof of free tartaric acid in the wine. Free sulphuric acid may be detected by means of the quinine test described in the article on Vinegar.

A strip of filter paper steeped for several hours in wine, and then dried, is brittle if either acid-potassium-sulphate, or free sulphuric acid is present.

The principal volatile acid is acetic, but it is always accompanied by formic, propionic, butyric, and other members of the same series. The general method of estimation is to take from 10 to 20 cc. of the wine suitably diluted, and titrate with d. n. soda, using tincture of logwood as an indicator, the result being the *total acidity.* On now evaporating the wine on the water-bath to a syrupy extract, diluting and again titrating, the loss of acidity corresponds to the *volatile acid,* the latter being expressed in terms of acetic acid, the non-volatile as tartaric acid. L. Weigert* has shown that by distilling in a vacuum, the whole of the acetic acid can be obtained; 40 or 50 cc. of the wine are in this way boiled to dryness, water added to the dry residue, and the process thrice repeated.

A very different and highly ingenious method of diagnosing and estimating volatile acids has been proposed by E. Duclaux. As this is applicable not to wines alone, but also to beers, sour milk, and in fact to all liquids developing acids of the acetic series, it will be described at length.

* *Zeitsch. für Analyt. Chemie,* 1879, 207.

§ 280. *Estimation of Volatile Acids by the Method of E. Duclaux.*—The process depends upon the regularity with which the different volatile acids distil. If in a retort of from 250 to 300 cc. be introduced 110 cc. of a mixture of acetic acid and water, and 100 cc. (that is $\frac{10}{11}$) be distilled, the quantity of acid which has come over is found to be 80 per cent. of the whole, or very nearly so. Further, if the 100 cc. be successively titrated, in every 10 cc. the successive numbers thus obtained (indicating the proportion of acid passing in these equal volumes) are the same, whatever may be the quantity of acid operated upon, provided the acid is pure; but it *varies very sensibly should there exist even feeble traces of the fatty acids.* It is then sufficient to study the course of the distillation of the acids in order to know their nature. In a general way, foreign matters exercise only a slight influence; but it is always best to eliminate them as far as possible by operating on a first or second distillation.

For the titration, M. Duclaux uses lime-water standardised by sulphuric acid. The size of the retort does not exercise the great influence which might be expected; but it is well to use one of about 300 cc. capacity, for the experiments on which the tables are founded were conducted in retorts which varied from between 250 to 350 cc. The slight difference in the results from a retort of 800 cc., as compared with one of 300 cc., may be gathered from the following table, which represents the distillation of 110 cc. of a dilute acetic acid.

The two series of numbers, A and B, are obtained by titrating each 10 cc., until 100 cc. have come over; the acetic acid in the A series being worked out in percentage of the whole acid found in the entire distillate, and that in the B series in the quantity of acid existing in the retort.

ESTIMATION OF ACETIC ACID.

	Retort of 800 cc.		Retort of 300 cc.	
	A.	B.	A.	B.
1.	7·2	5·5	7·4	5·9
2.	14·7	11·2	15·3	12·2
3.	22·7	16·9	23·5	18·7
4.	31·2	23·7	32·1	25·6
5.	40·2	30·6	41·2	32·9
6.	49·9	32·9	50·9	40·6
7.	60·2	45·8	61·3	48·9
8.	71·9	54·7	72·5	57·9
9.	85·3	64·8	85·2	67·9
10.	100·0	75·9	100·0	79·8

It would appear that the quantity of acid which vaporises at a given moment, is proportional to that which exists in

that same moment in the heated liquid; and when the quantities of water distilled increase in an arithmetical progression, the quantities of acid increase in a geometrical progression.

Let y be the quantity of acid existing at any moment in the volume λ of the liquid remaining in the retort; the quantity of acid dy, which will volatilise with the volume $d\lambda$ of the liquid will be evidently first proportional to $d\lambda$ and then to y. Thus—

$$dy = xy d\lambda,$$

whence may be educed (calling y the total weight of acid existing at the commencement in the volume L of the liquid),

$$ly - lY = l\frac{y}{Y} = -K(L - \lambda)$$

giving

$$y = Ye^{-x(L-\lambda)}$$

Let a be called the quantity $Y - y$ of acid which distils when

$$L - \lambda = l = L\frac{l}{L}$$

has been removed from the liquid; then we have

$$a = Y1 - e\left(\frac{-xLl}{L}\right) = Y\left(1 - e^{-m\frac{l}{L}}\right)$$

The following table shows that acetic acid obeys this law; the figures in the second column are calculated by the formula

$$a = 102\left(e^{\frac{0{\cdot}0615l}{11}} - 1\right)$$

	a found.	a calculated.		a found.	a calculated.
1.	5·9	5·2	6.	40·5	40·5
2.	12·2	12·2	7.	48·7	48·7
3.	18·8	18·7	8.	57·9	57·8
4.	25·6	25·4	9.	67·7	66·6
5.	32·9	32·7	10.	79·8	76·3

Butyric acid obeys the same law; but it has a method of distillation in some sense inverse to that of acetic acid, and passes in greater abundance in the first portions. The following table gives the experimental and the calculated numbers found in distilling a mixture of butyric acid and water, in the manner before described.

The formula for calculation is—

$$147 \cdot 5\left(1 - e\frac{-0131l}{11}\right)$$

	A.	B.	B calculated.
1.	16·8	16·1	16·8
2.	31·9	31·1	31·4
3.	45·4	44·3	44·4
4.	57·7	56·1	55·8
5.	67·9	66·2	66·1
6.	77·2	75·3	75·1
7.	85·0	82·9	83·2
8.	91·4	89·2	90·3
9.	96·4	94·0	96·6
10.	100·0	97·5	102·4

It is thus seen that the numbers are very different from those of acetic acid, and that nearly the whole of the acid is obtained.

Propionic acid.—Formula for calculation—

$$m = 357\left(1 - e\frac{-0 \cdot 033l}{11}\right)$$

	A.	B.	B calculated.
1.	11·3	10·5	10·8
2.	22·8	21·1	21·4
3.	34·0	31·5	31·5
4.	44·6	41·4	41·4
5.	55·3	51·3	51·1
6.	65·4	60·6	60·3
7.	74·7	69·5	69·3
8.	84·0	78·0	78·0
9.	92·5	85·8	86·5
10.	100·0	92·8	95·3

Valerianic Acid.—

	B.		B.
1.	24·5	6.	85·7
2.	44·5	7.	89·7
3.	59·5	8.	92·8
4.	71·3	9.	95·4
5.	79·5	10.	96·9

Formic Acid.—

$$f = 30 \cdot 2\left(e\frac{0 \cdot 1194l}{11} - 1\right)$$

	A.	B.	B calculated.
1.	5·5	3·5	3·5
2.	11·9	7·6	7·3
3.	18·5	11·8	11·6
4.	25·7	16·3	16·3
5.	34·0	21·6	21·6
6.	43·1	27·3	27·5
7.	53·1	33·7	34·1
8.	65·2	41·4	41·4
9.	79·8	50·7	49·7
10.	100·0	63·5	58·8

Passing from the single acids to the behaviour of mixed volatile acids, it is found that each acid distils in the same proportion as if it existed individually in the liquid. Thus Duclaux found a mixture of equivalent quantities of butyric and acetic acids behave as follows:—

	A.	B.	B calculated.
1. . .	12·7	11·4	11·4
2. . .	24·8	22·1	22·1
3. . .	35·9	32·0	32·1
4. . .	46·4	41·4	41·6
5. . .	56·3	50·3	50·5
6. . .	65·7	58·6	58·9
7. . .	74·5	66·4	67·0
8. . .	83·1	74·1	74·4
9. . .	91·4	81·6	82·2
10. . .	100·0	89·3	90·0

A mixture of 2 of butyric to 1 of acetic acid, when distilled, gave the following series:—

	A.	B.	B calculated.
1. . .	14·0	12·8	12·8
2. . .	26·1	25·1	24·8
3. . .	35·5	36·2	35·9
4. . .	50·6	46·4	46·1
5. . .	60·6	55·5	55·3
6. . .	69·8	63·9	63·9
7. . .	78·4	71·7	71·8
8. . .	86·0	78·7	79·1
9. . .	93·1	85·2	85·6
10. . .	100·0	91·6	92·0

Hence it follows, that it is possible to obtain from fractional distillation a knowledge of the nature and quantity of the volatile acids existing in the liquid. Theoretically, ten different equations might be educed, and ten volatile acids determined; but in practice this is not possible; and should there be even three volatile acids, it is better to make a new distillation after a partial saturation, which will almost completely arrest one of the acids, and let only two pass into the receiver.

As an example of the method of calculation, the following table gives the results of the distillation of a certain wine, A and B having the same signification as before:—

	A.	B.	M.	N.
1. . .	9·6	8·6	1·2	3·2
2. . .	19·2	17·3	1·1	3·1
3. . .	28·8	26·0	1·0	3·0
4. . .	38·4	34·7	1·0	2·8
5. . .	48·2	43·5	1·0	2·5
6. . .	57·9	52·2	1·0	2·5
7. . .	67·8	61·1	1·0	2·2
8. . .	77·9	70·2	1·0	2·1
9. . .	88·5	79·9	1·0	1·6
10. . .	100·0	90·2	1·1	1·3

From the B series there should be acetic acid mixed with either propionic or butyric acids. In order to know which of the two is present, a double calculation is necessary. Turning to the tables giving the numbers obtained for the first 10 cc. in the distillation of pure acetic and pure propionic acids (pp. 450 and 451), we find for the former 5·2, for the latter 10·5; then, by the following equation, the numbers in the column M are obtained—

$$8{\cdot}6x + y = 5{\cdot}2x + 10{\cdot}5y$$

$$\frac{y}{x} = 1{\cdot}2$$

Analogous calculations give for $\frac{y}{x}$ the series of numbers contained in N, if butyric acid is thought to be present; it now becomes evident, that the mixture was formed of equivalent parts of acetic and propionic acid. In order, however, to avoid long calculations, it is better to make tables of reference with various mixtures, so that in most experiments the quantities will fall somewhere near those given in the tables, and at all events be a guide. In the following tables A and B have the same signification as before, and 110 cc. are supposed to be distilled in the manner described, in a retort of about 300 cc. capacity :—

TABLE XLVI.—Mixtures of Acetic Acid (a) and Propionic Acid (m).

	$\frac{a}{m} = \frac{668}{326} = \frac{2}{1}$		$\frac{a}{m} = \frac{334}{326} = \frac{1}{1}$	
	A.	B.	A.	B.
1. . .	9·1	7·7	9·7	8·5
2. . .	18·4	15·6	19·4	17·0
3. . .	27·8	23·6	29·2	25·6
4. . .	37·3	31·6	38·9	34·1
5. . .	46·9	39·8	48·6	42·7
6. . .	56·6	48·0	58·6	51·4
7. . .	66·6	56·5	68·5	60·1
8. . .	77·0	65·2	78·6	68·9
9. . .	88·0	74·6	89·1	78·2
10. . .	100·0	84·8	100·0	87·7

TABLE XLVII.—A MIXTURE OF ACETIC (a), AND BUTYRIC ACID (b).

	$\frac{a}{b}=\frac{564}{28}=\frac{20}{1}$		$\frac{a}{b}=\frac{10}{1}$		$\frac{a}{b}=\frac{840}{168}=\frac{5}{1}$		$\frac{a}{b}=\frac{4}{1}$		$\frac{a}{b}=\frac{2}{1}$		$\frac{a}{b}=\frac{34}{35}=\frac{1}{1}$		$\frac{a}{b}=\frac{796}{582}=\frac{1}{2}$		$\frac{a}{b}=\frac{1}{4}$	
	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
1. .	7·9	6·4	8·6	7·0	9·5	7·9	9·8	8·2	11·3	9·6	12·7	11·4	14·0	12·8	15·5	14·5
2. .	16·3	13·2	17·4	14·2	19·0	15·8	19·5	16·2	22·0	18·9	24·8	22·1	26·1	25·1	29·5	27·7
3. .	24·8	20·1	26·2	21·4	28·3	23·6	29·1	24·2	32·4	27·8	35·9	32·0	39·5	36·2	42·2	39·5
4. .	33·6	27·2	35·2	28·8	37·7	31·4	38·5	32·1	42·3	36·3	46·4	41·4	50·6	46·4	53·6	51·2
5. .	42·7	34·5	44·5	36·3	47·1	39·2	47·8	39·8	52·2	44·7	56·3	50·3	60·6	55·5	63·9	59·9
6. .	52·2	42·2	54·1	44·1	56·6	46·1	57·5	47·8	61·4	52·7	65·7	58·6	69·8	63·9	73·1	68·6
7. .	62·2	50·4	64·1	52·3	66·3	55·3	67·0	55·7	70·7	60·6	74·5	66·4	78·4	71·7	81·2	76·2
8. .	73·1	59·2	74·8	61·1	76·5	63·8	77·0	64·1	79·9	68·5	83·1	74·1	86·0	78·7	88·3	82·8
9. .	85·4	69·2	86·4	70·6	87·4	72·9	87·9	73·1	89·4	76·7	91·4	81·6	93·1	85·2	94·5	88·6
10. .	100·0	81·0	100·	81·7	100·	83·4	100·	83·3	100·	85·8	100·	89.3	100·	91·6	100·	93·8

TABLE XLVIII.—MIXTURES OF ACETIC ACID (a), OR OF BUTYRIC ACID (b), WITH VALERIANIC ACID (v).

	$\frac{a}{v}=\frac{593}{118}=\frac{5}{1}$		$\frac{a}{v}=\frac{296}{236}=\frac{5}{4}$		$\frac{b}{v}=\frac{291}{236}=\frac{5}{4}$	
	A.	B.	A.	B.	A.	B.
1. . .	11·1	9·1	16·3	14·3	20·6	20·0
2. . .	20·8	17·2	30·3	26·5	38·3	37·0
3. . .	30·5	25·1	42·4	37·0	52·9	51·0
4. . .	39·9	32·8	52·5	45·9	64·6	62·4
5. . .	48·9	40·3	61·3	53·6	74·5	71·9
6. . .	57·9	47·7	69·3	60·5	82·1	79·3
7. . .	67·2	55·4	76·6	66·9	88·2	85·2
8. . .	77·0	63·4	84·0	73·4	93·2	90·0
9. . .	87·5	72·2	91·5	80·0	96·9	93·3
10. . .	100·0	82·4	100·0	87·4	100·0	96·8

TABLE XLIX.—MIXTURES OF ACETIC ACID (a) WITH FORMIC ACID (f).

	$\frac{a}{f}=\frac{593}{293}=\frac{2}{1}$		$\frac{a}{f}=\frac{296}{293}=\frac{1}{1}$		$\frac{a}{f}=\frac{296}{586}=\frac{1}{2}$	
	A.	B.	A.	B.	A.	B.
1. . .	6·6	4·9	6·1	4·3	6·0	4·1
2. . .	14·0	10·4	13·5	9·5	13·2	9·2
3. . .	22·1	16·3	21·1	14·8	20·6	14·3
4. . .	30·2	22·3	28·9	20·3	28·6	19·9
5. . .	39·1	28·9	37·8	26·6	37·1	25·7
6. . .	48·5	35·9	43·8	33·0	46·4	32·2
7. . .	59·2	43·8	57·2	40·3	56·5	39·3
8. . .	70·6	52·3	68·9	48·5	68·4	47·5
9. . .	83·8	62·0	82·7	58·2	81·9	56·9
10. . .	100·0	74·0	100·0	70·4	100·0	69·4

It now only remains to apply the preceding principles to the examination of wines. 275, or 550, or 825 cc., according as the wine is more or less rich in alcohol, is agitated strongly (or a current of air passed through the liquid), in order to free it from carbonic acid gas. It is next distilled to ten-elevenths, air drawn through the apparatus, and the distillate titrated by lime-water. A slight excess of lime-water is next added, and the

liquid is concentrated by evaporation to about 250 cc., in order to get rid of the alcohol; 1 grm. of glycerine is now added, and sufficient tartaric acid to put the fatty acids at liberty.

The tartrate of lime is allowed to crystallise, and the liquid decanted and made up with the washing water to 275 cc., after having added sufficient tartaric acid to ensure that on completion of the distillation, the residue will be nearly as acid as at the end of the first operation—1 grm. of tartaric acid per litre suffices for this. The liquid is now distilled anew to ten-elevenths, and the whole distillate titrated; the relation between the quantity of lime-water necessary now, and that of the first saturation, will serve to show the quantity of volatile acid existing in the wine in question.

This new liquid is submitted to the same operations as before, adding nothing save the quantity of tartaric acid exactly necessary. The acid liquid is made up to 165 cc., of which 150 cc. are distilled over, 50 cc. out of the 150 cc. are titrated, the remaining 100 are made up to 110 cc. with water, and submitted to fractional distillation, titrating every 10 cc. of the distillate. The numbers found will conduct directly, by a simple calculation, to the knowledge of the quantity and nature of the volatile acids in the wine. Thus, taking a wine, the results of the distillation of which are given in a tabular form at p. 452:—

275 cc. of this wine were distilled to 250 cc.; these 250 cc. required for neutralisation 316 cc. of lime-water of 30·6 [*i.e.*, 30·6 cc. = 0·075 acid acetic]; the second distillation has given 83·2 per cent. of the acid employed. Hence, for 275 cc.

$$316 \text{ cc.} \times \frac{100}{263} = 379 \text{ cc. of lime-water.}$$

The third and last distillation showed in the liquid equal parts of acetic and propionic acids; the proportions in which these acids pass over are, as has been shown, $\frac{93}{80}$; hence the third and last distillate will contain 51·2 per cent. of the total acetic acid present in the wine, and 80·4 per cent. of the total propionic acid, $\frac{80\cdot4}{51\cdot2}$ = in equivalents 100 to 637 propionic acid, or $\frac{100}{164}$, therefore $\frac{100}{164}$ of 379 cc. or 231 cc. was neutralised by acetic acid, and the remainder by propionic.

In order to discover, by this method, valerianic acid, which, it would appear, exists in many sound wines (in about the proportion of 6 mgrms. per litre), it is necessary to distil a considerable quantity of wine, and then to saturate the distillate to nine-tenths or nineteen-twentieths. In this way, acetic and

valerianic acid pass almost alone into the receiver. For instance, 7·7 litres of the wine alluded to before (p. 452) were distilled, and 10 grms. of lime salts obtained; sulphuric acid was added, representing nearly one-fortieth of the lime salt, and then the partially-decomposed salt distilled, when the following numbers were obtained:—

	A.	B.	$\frac{a}{b}$
1.	10·5	8·7	6·1
2.	20·5	16·9	6·1
3.	29·3	24·1	6·8
4.	38·1	31·4	6·9
5.	46·8	38·6	7·2
6.	55·6	45·9	7·5
7.	64·8	53·4	7·4
8.	75·2	62·0	7·5
9.	86·6	71·4	6·5
10.	100·0	82·4	6·0

The numbers in the columns A and B correspond in no way to mixtures of acetic acid with butyric or propionic. With valerianic acid, on the contrary, there is a relation constant enough, as the fourth column shows, the slight irregularities arising probably from a trace of butyric acid.

§ 281. *Estimation of Tartaric Acid and Bitartrate of Potash.*—This is best estimated by the method suggested by Berthelot:—20 cc. of wine are mixed with 100 cc. of equal volumes of alcohol and ether in a well-stoppered flask. The same process is employed to another 20 cc., but with the addition of potash in sufficient quantity to neutralise about one-fifth of the free acid present. Both bottles are allowed to stand two or three days, and at the end of the time, owing to the insolubility of bitartrate of potash in strong alcohol, there will be a deposit of that salt in both bottles. The first will represent the bitartrate of potash present as such; the second, the whole of the tartaric acid which the wine contains. There is, however, always a small quantity of bitartrate in solution, about ·004 grm., equalling ·21 d. n. soda, and this amount must be added to that found. The precipitates from both bottles are collected on separate filters, washed with the alcohol-ether mixture, dissolved in water, and titrated with soda solution.

Direct Estimation of Malic Acid.—100 cc. of wine are precipitated with lime-water, added only in slight excess; the filtrate is evaporated down to one-half, and absolute alcohol added in excess; the resulting precipitate, consisting of malate and sulphate of lime, is then collected on a filter, washed, and weighed.

If, now, the sulphate of lime in this sample be estimated by solution in water, and precipitation of the sulphuric acid by baric chloride, &c., and the amount subtracted from the total weight of the precipitate, the remainder equals malate of lime.

5. *Estimation of Ethers in Wine.*—The compound ethers in wine may be divided into volatile and non-volatile. It is especially the volatile ethers that impart a character to the wine, and give it bouquet and odour. The proportion of volatile to fixed ethers is very small in unfortified wines, but the reverse is the case with fortified wines. The total amount of ethers is extremely small; Dr. Dupré gives about one part of compound ether in 300 parts of wine as the highest proportion he has yet met with. The ethers themselves are, of course, derived from conversion of the alcohols, the ultimate amount depending entirely on the relative proportion of alcohols, acid, and water present, and not being dependent on the *nature* of the alcohols or acids. If, as sometimes happens, an excess of compound ether is added to a wine, decomposition will at once begin, until ultimately the wine will contain no more than it would otherwise have reached in the natural order of things. An estimation of the ethers is, therefore, of the greatest possible importance, as it enables the analyst to judge of the age, character, &c., of the wine.

Berthelot has given the following formula for the calculation of the amount of alcohol present in the compound ethers of wine:—

$$y = 1{\cdot}17\ \text{A} + 2{\cdot}8$$
$$x = \frac{y \times a}{100}$$

A is the percentage of alcohol by weight in the wine; *a* the amount of alcohol equivalent to the total free acid (reckoned as acetic) contained in 1 litre. It hence follows that if the amount of alcohol present as ether, found by experiment, fairly agrees with the calculated amount, etherification is complete, and the wine must be of a certain age; if the compound ethers exceed the proper amount, the probability is that it is an artificial wine; and, lastly, if the amount of ethers is below the theoretical standard, either etherification is not complete, on account of its youth, or alcohol has been recently added.

Dr. Dupré, taking advantage of the fact that all ethers (when treated with an alkali) break up into their respective acid and

alcohol, indirectly estimates both the volatile and non-volatile ethers as follows:—

250 cc. of wine are distilled, with special precautions against loss, until 200 cc. have come over; the distillate is now made up to 250 cc., and 100 cc. of this titrated. Another 100 cc. are decomposed by alkali (a known amount), and again titrated. The second 100 cc. will, of course, be more acid than the first, and therefore the amount of *volatile* ether can be estimated from such increase. The *fixed* ether is determined by evaporating down to 50 or 60 cc. in an open dish on the water-bath; the residue, which, of course, contains *no alcohol*, is rendered alkaline with sodium hydrate, some tannin added, and the whole slowly distilled; the fixed ether present is resolved into an acid and an alcohol, and the latter distilled over; the distillate is rendered slightly acid by sulphuric acid, redistilled, and the second distillate (which may amount to 20 or 25 cc.) oxidised into acetic acid in a closed flask by potassic bichromate; the acetic acid is distilled over and titrated.

6. *The Estimation of Sugar in Wine* is carried out on the principles described at p. 113 *et seq.*

7. *Albuminoid Substances.*—The albuminoid substances in wine may be estimated by Mr. Wanklyn's well-known ammonia process:—5 cc. of the wine are put in a half-litre flask, and made up with water to 500 cc.: $\frac{1}{100}$ (*i.e.*, 5 cc.) of this is distilled with a little water and pure carbonate of soda (ammonia free), and the ammonia in the distillate estimated by the colorimetric process known as Nesslerising. An alkaline solution of permanganate of potash is then added, and the operation repeated—the ammonia coming over now being the result of the breaking-up of albuminoid bodies. It would appear that in *white* wines, the albuminous matters are very small in amount; while in *red*, and most *young* wines, there is an excess of albuminous matters, which decreases with age; hence, in experienced hands, a determination of this kind may help to distinguish between old and new.

Thudichum and Dupré found in certain wines the following amounts of ammonia:—

	Ammonia free. Per cent.	Ammonia albd. Per cent.
Ingelheimer, red,	0·0051	0·3730
Port, 1851,	0·0046	0·0888
Sherry, 30 years in bottle,	0·0073	0·1807
Madeira,	0·0021	0·1581
Merstemer,	0·0021	0·3550
Natural Port,	0·0019	0·0527
Port, 1865,	0·0012	0·1760

8. *The tannin* of wine may be estimated by the methods described at p. 332 *et seq.*

§ 282. 9. *Estimation of the Colouring-matter of Wine.*—The colouring-matter of red wines has been termed *œnolin*, or *œnocyanin*, and has also received other names. Glenard has assigned to it the formula $C_{10}H_{10}O_5$; but it is doubtful whether it has ever yet been separated in a state of absolute purity. The process used by Glenard was—precipitation with lead acetate, exhaustion of the washed, dried, and powdered precipitate, first, with anhydrous ether saturated with HCl, then with pure ether; and, lastly, extraction with alcohol, from which the œnolin was obtained by evaporation as a bluish-black powder insoluble in ether, almost insoluble in pure water, but more readily dissolved in acidulated water, acidulated alcohol dissolving it easily. The blue colour is turned red by acid. Œnolin, according to Vaserine,* may be separated from wine by mixing the latter with lime to the consistency of a paste, which is drained on a funnel. The residue, containing the colouring-matter, is mixed with alcohol of 95 per cent., and treated with sufficient sulphuric acid to neutralise the lime and decompose the compound of lime with the colouring-matter. The solution is filtered from calcium sulphate, and on evaporation leaves œnolin as a black powder. Solutions of œnolin show, when examined by the spectroscope, certain bands, and the application of this instrument to the investigation of wines is indispensable. In no case, however, should the analyst trust entirely to descriptions or plates; the only safe course is to have in readiness tinctures of colouring-matters of different strength and different ages, as well as samples of wine artificially coloured.

The colour of white wines is due to oxidised tannin; it takes long to develop; hence the manufacturer not unfrequently adds a little caramel. Should this be the only addition, it would be injudicious to consider the wine adulterated.

The artificial colouring of wines by elder-berry, logwood, cochineal, aniline, &c.,† is said to exist, at all events, on the

* *Bull. Soc. Chim.* [2], xxix. 109, 110.

† Soubeiran says: "At Fismes, in the neighbourhood of Rheims, there has been manufactured for more than a century (since 1741) a colouring agent composed of elder-berries, alum, and water, in different proportions, the prolonged use of which can only have injurious consequences on the health, on account of the alum. Unfortunately, the production of this colouring agent (*teinte*) was encouraged by a royal decree of 1781. . . . Recent analyses have shown that this *liqueur de Fismes* contains from 20·8 to 57·56 grms. per litre of alum.—"Dict. des Falsifications." Paris, 1874.

Continent; and it is a fact that a few home-made, low-priced, wines, almost entirely fictitious, are passed off by the aid of the same or similar substances; but with regard to the ordinary foreign wines in English commerce, there is no reliable evidence whatever that any adulteration of this kind has been practised. Nevertheless, it is absolutely necessary to be acquainted with the best and most recent methods for the discovery of such frauds.

Dr. Dupré, taking advantage of the fact that the colouring-matter of wine* only dialyses to a minute extent, and that the colouring-matters of Brazil, logwood and cochineal readily dialyse, separates the latter colouring-matters from the wine by dialysis. The same chemist has suggested a still more convenient and practical process—viz., the staining of a jelly. The jelly is made by dissolving 5 grms. of gelatine in 100 cc. of warm water, and pouring the solution into a square flat mould made of paper. From this cake cubes about $\frac{3}{4}$ inch square are cut with a sharp wet knife, and are immersed in the wine, taken out after the lapse of from twenty-four to forty-eight hours, washed slightly, and sections cut, in order to see how far the colouring principles have penetrated. If the wine is pure, the colour will be confined almost entirely to the edges of the slice, or will not have penetrated beyond $\frac{1}{10}$ to $\frac{1}{8}$ inch; most other colouring-matters rapidly permeate and colour the jelly.

(1.) *Colouring-matters penetrating slowly into the jelly:*

Colouring-matter of pure wine.
" " Rhatany root.

(2.) *Colouring-matters penetrating rapidly into the jelly:*

Rosaniline.	Litmus.
Cochineal.	Red Cabbage.
Logwood.	Beetroot.
Brazil-wood.	*Malva sylvestris.*
Indigo.	*Althea officinalis.*

The jelly may be examined spectroscopically, good results being obtained in the case of rosaniline, red cabbage, and beetroot; and may be also tested with reagents—*e.g.*, dilute ammonia dissolves much colour from the slice, if the colour should be derived from logwood or cochineal; on the other hand, the

* The colouring-matter of Rhatany root has the same property.

ammonia remains colourless in the case of rosaniline, red cabbage, and beetroot.

A simple method for the detection of certain colouring-matters is that of Lammatine:—Shake 100 parts of the wine with 100 of coarsely-powdered peroxide of manganese, and then pass through a double filter; if pure, a colourless filtrate will result. The process is said to answer well in the case of logwood and cochineal, but to fail with aniline.

A general method, applicable to fucshine and other colouring-matters, is based upon the fact that a great many of the colouring-matters which may be used for purposes of wine adulteration (such as caramels, ammoniacal cochineal, sulphindigotic acid, logwood, and the lichen reds), are precipitated by acetate of lead; whilst fuchsine, if present in considerable quantity, is only partially thrown down. Those which are not precipitated may be separated by agitating the filtrate with amyl alcohol.

The lead precipitate may be treated by dissolving out cochineal, sulphindigotic acid, and fuchsine, by a solution of potassic carbonate [2 : 100]. From this liquid the fuchsine is separated by neutralisation with acetic acid and agitation with amyl alcohol, the rose-coloured liquid obtained being identified as a solution of fuchsine by the spectroscope. On now acidifying the liquid with sulphuric acid, the carminamic acid from the cochineal is removed by means of amyl alcohol, and identified by its three bands—viz., one between D and E in the red, the second in the green, and the third in the blue. The indigo remaining may be detected by the blue colour, and absorption-band between C and D. The original lead-precipitate, insoluble in potassic carbonate, is treated with a two per cent. solution of potassium sulphide, which dissolves the colouring-matter of logwood and that of the wine itself. Logwood may, however, be tested for directly in the wine by the addition of calcium carbonate and two or three drops of lime-water. In the case of a natural wine, the filtered liquid is almost colourless, but is of a fine red colour if logwood is present. Lastly, the lichen red may be obtained by washing the insoluble portion left after treatment with potassium sulphide, and dissolving it in alcohol, when a red colour and a definite absorption-band reveal its presence.

For the detection of fuchsine simply, Bouillon (*Comptes rendus*, lxxxiii. 858, 859) recommends half a litre of the wine to be evaporated down to 120 cc., with the addition of 20 grms. of barium hydrate. It is then filtered, and the filtrate shaken up with ether; the ether is separated, a drop of acetic acid, a little

water, and a small piece of white silk, are added, and (if an appreciable amount of fuchsine is present) the silk assumes a pink colour immediately; if not, the liquid must be concentrated nearly to dryness.

F. König* has a process for detecting fuchsine: 50 cc. of the wine are treated with ammonia in slight excess, and boiled with a little pure wool [·5 grm.], until all the alcohol and ammonia are evaporated. The wool is washed and directly moistened with strong potash, and heated until it dissolves into a more or less brown fluid. After cooling, to this is added half its volume of pure alcohol, and then an equal volume of ether; it is strongly shaken. The smallest trace of fuchsine is taken up by the ether, and is coloured red by acetic acid. 0·4 mgrm. fuchsine in a litre of wine is said by this means to be discovered readily. The process destroys the natural colour of the wine.

§ 283. Vogel and others have studied the detection of the colouring-matters of wine by means of the spectroscope.

The following curves are examples of various colouring-matters (see fig 45):—

No. 37. Wine colouring-matter, (I.) pure, (II.) diluted.

No. 38. Wine colouring-matter, with ammonia.

No. 39. (I.) Mallow colouring-matter concentrated, (II.) elderberry concentrated.

Fig. 45.

No. 40. Acid cherry. (*b*) Acid cherry with the addition of tannin.

No. 41. Mallow colouring-matter with the addition of alum.

No. 42. Indigo solution.

With carefully made comparison solutions, there can be little doubt that the spectroscopical method of identifying colouring-matters will be found of great value.

Lastly, M. A. Gautier† has proposed a method aiming at a systematic detection of every probable colouring-matter likely to be added to wine. How far the whole, or any portion, of this elaborate system will be followed and confirmed by chemists remains to be seen.

The following abstract of M. Gautier's paper is taken from the *Analyst*, i., 1877:—

* *Ber. der deutsch. Chem. Gesellsch.*, *Berlin*, xiii. 2263.

† *Bull. Soc. Chim.*

M. Gautier's Process for Detecting Colouring-Matters in Wine.

§ 284. *Preliminary Preparation of the Sample.*—The wine to be examined is mixed with one-tenth its volume of white-of-egg previously diluted with one and a half times its bulk of water, well shaken, and, after standing for half an hour, filtered. If the wine is very poor in tannates, a few drops of a fresh aqueous solution of tannin should be added previous to the agitation with albumen. The filtrate is treated with dilute sodium bicarbonate until its reaction is *very* feebly acid. All the reactions of Table B. must be made on this liquid, except those for indigo, which are executed upon the albuminous precipitate.

Table B.—Systematic process to be followed for the detection of the nature of foreign colouring-matters added to wines.

A. Having placed aside the filtrate from the albuminous precipitate, the precipitate is washed until the washings are almost colourless.

Two cases may present themselves:—

(*a.*) The precipitate after washing remains wine-coloured, lilac, or maroon; *wine, natural, or adulterated with the greater part of the substances usually employed.* Pass on to C.

(*b.*) The precipitate is of a very deep wine-colour, violet-blue, or bluish; *wines from the deepest coloured grapes, or wines coloured with indigo.* Proceed to B.

B. The precipitate is washed with water, then with alcohol of 25 per cent., a part is then removed and boiled with alcohol of 85 per cent.

(*a.*) The filtrate is *rose*, or *wine-coloured.* A portion of the precipitate is removed from the filter, suspended in water, and carefully saturated with dilute potassium carbonate. The colour changes to brown or blackish-brown; *natural wines, or adulterated with substances other than indigo.* Pass to C.

(*b.*) The filtrate is *blue.* A portion of the precipitate suspended in water and treated with dilute potassium carbonate affords a deep blue liquid, which changes to yellow by an excess of the reagent. *Various preparations of indigo. Indigo.*

C. 2 cc. of wine are treated with 6 to 8 cc of a $\frac{1}{200}$ solution of sodium carbonate, which must be added in slight excess (1 cc.) after the change of colour.

(*a.*) The liquid becomes *lilac*, or *violet*, sometimes the liquid becomes only winey, or dashed with violet. *Brazil-wood, cochineal, Portugal berries, fuchsine* . . . . . *wines of certain sorts, fresh beetroot, logwood, both elders, whortleberries* (myrtille), *Portugal berries.* Pass to D.

(*b.*) The liquid becomes bluish-green, sometimes with a faint lilac tint, *wine, hollyhock, privet, whortleberries, logwood, Portugal berries, fuchsine.* Pass to M.

(*c.*) The liquid becomes greenish-yellow without any blue or violet, *beetroot* (old or fermented decoction), *whortleberries, certain rare varieties of wine.* Pass to L.

D. The liquid C. (*a.*) is heated to boiling.

(*a.*) The liquid remains wine-violet, rose, or wine-lilac, or becomes a brighter lilac; *logwood, Brazil-wood, cochineal, certain varieties of wine.* Pass to E.

(*b.*) The colour disappears, or changes to a yellow, or maroon, or reddish tint, *wine, fuchsine, both elders; whortleberries, Portugal berries, fresh beetroot.* Pass to F.

E. Treat 4 cc. of the wine with 2 cc. of each of a 10 per cent. solution of alum, and a 10 per cent. solution of crystallised sodium carbonate. Filter.

(*a.*) Clear yellowish-green lake (which may be bluish from mixtures of wines containing maroon), filtrate colourless, becoming very slightly yellow on warming; its own volume of aluminium acetate at 2° B. almost wholly decolourises it. On acidification with acetic acid, after treatment with its own volume of barium-hydrate (saturated solution), the wine becomes clear greenish-yellow or maroon, *pure or mixed* wines. See Table A.

(*b.*) Greenish-blue lake, or dirty yellowish-green, according to the varieties present, sometimes very slightly winey. Filtrate bright-rose, gradually decolourised on warming, though retaining a tinge of lilac; not decolourised by lime-water in the cold. COCHINEAL.

(*c.*) Winey-violet lake, which darkens on exposure to the air. Filtrate bottle-green, or grey faintly red (if much logwood is present). The filtrate becomes green on warming. LOGWOOD.

(*d.*) Lilac, or maroon-lilac lake. Filtrate greyish with tint of maroon. On boiling, this filtrate becomes fine old-wine coloured. BRAZIL-WOOD.

F. Treat 4 cc. of the wine with alum and sodium carbonate (as explained at E.), add to the mixture two or three drops of very dilute sodium carbonate, and filter.

(*a.*) The filtrate is lilac or winey, *Portugal berries, fresh beetroot.* Pass to G.

(*b.*) The filtrate is bottle-green, or reddish-green, *wine, fuchsine, black elder, whortleberries, beetroot.* Pass to H.

G. Treat 2 cc. of the wine with subacetate of lead solution, of density 15° B. Shake. Filter.

(*a.*) The filtrate is rose, which persists even when made slightly alkaline; it slowly disappears on boiling. Lime-water destroys the rose colour. PORTUGAL BERRIES.

(*b.*) The filtrate is yellowish, or brownish-red. FRESH BEETROOT.

H. The alum-lake obtained from F. (*b.*) is—

(*a.*) Deep blue. On treating the clarified wine with a few drops of aluminium acetate solution, it becomes a decided violet, or wine violet. *Both elders.* Pass to I.

(*b.*) Bluish-green, green, or faintly rose-tinted, *wine whortleberries, beetroot, fuchsine.* Pass to J.

I. After the test H. (*a.*) treat a fresh quantity of 2 cc. with 1·5 to 2 cc. (according to its acidity and the depth of its colour) of an 8 per cent. solution of sodium bicarbonate charged with carbonic acid.

(*a.*) The liquid remains lilac for a moment, then changes to greenish-grey blue. Another specimen treated with sodium carbonate (according to C.), and heated to boiling, becomes dark greenish-grey. BLACK ELDER.

(*b.*) The liquid retains a lilac tint, or becomes grey with mixture of maroon, or dirty lilac. Another specimen treated with sodium carbonate (as at C.) tends to discolour on heating, the green being replaced by red. DWARF ELDER.

J. Treat 5 cc. of the clarified wine with a slight excess of ammonia, heat to boiling, and after cooling shake with 10 cc. of ether, decant and evaporate the ether, and treat the residue left on evaporation with acetic acid.

(*a.*) The liquid becomes red. FUCHSINE.

(*b.*) The liquid does not become red, *wine, whortleberries, fresh beetroot.* Pass to K.

K. Another specimen is treated according to C. with sodium carbonate.

(*a.*) The colour darkens or becomes red on heating, *whortleberries, fresh beetroot.* Pass to L.

(*b.*) The greenish or bluish-green liquid, possibly having a winey tinge, has a tendency to discolour on heating. *Natural wine.*

L. Treated with sodium bicarbonate according to the rules given at I.

(*a.*) The liquid is deep grey, slightly greenish, green, sometimes green with very slight lilac tint.

The clarified wine, treated with an equal volume of saturated baryta water, and filtered after standing for fifteen minutes, gives a dirty yellow, or slightly greenish filtrate.

With an equal volume of aluminium acetate of 2° B. it gives a lilac wine-coloured filtrate.

With a few drops of aluminate of potash no change of colour. With sodium carbonate, employed as at C., the liquid tends to lose its colour on heating. With barium peroxide, used according to Table A, column P, the liquid is faintly rose-tinted, with or without an orange-coloured deposit on the barium peroxide. NATURAL WINE.

With the general characters above indicated, if with baryta water it affords a madeira-coloured filtrate, changing to buff on acidulation with acetic acid; if with borax it becomes deep-green with a bluish cast; if with alum and sodium carbonate (as at E) a precipitate falls of a deep bottle-green, with bluish tinge, and if with aluminium acetate it remains rose-coloured with no change to violet-blue. TEINTURIER.

(*b.*) The liquid is reddish-yellow or brown-lilac. By treatment with acetate of alumina the filtrate is clear lilac. With a few drops of aluminate of potash the colour becomes that of the skin of an onion, and with a larger quantity of the reagent the colour is green, tinged with maroon. With sodium carbonate (employed as at C.) the fluid passes to yellowish or greyish-yellow, with tinge of red. With barium peroxide, flesh-coloured liquid with considerable orange-coloured deposit in contact with the peroxide. BEETROOT, *fermented or not.*

(*c.*) The liquid is yellowish-grey, with tinge of green or red. With baryta water the filtrate is yellowish olive-green. With aluminium acetate the filtrate is bluish-violet, or violet-lilac. With aluminate of potash, fresh rose, becoming yellowish-green, with an excess of reagent. With sodium carbonate (as at C.) the fluid becomes deep grey on heating. With barium peroxide the fluid is bleached, or remains but very slightly roseate, with a trace of orange deposit in contact with the peroxide. WHORTLEBERRIES.

M. The mixture of wine and alkaline carbonate C. (*b.*) is heated to boiling.

(*a.*) The mixture becomes lilac-violet, or violet. LOGWOOD.

(*b.*) The mixture tends to become decolourised, or changes to yellowish-green, or dark green, or maroon green, *natural wines, whortleberries, both elders, privet, Portugal berries, fuchsine.* Pass to N.

N. Treat the wine with alum and sodium carbonate, as directed at E., and filter.

(*a.*) The colour of the filtrate is lilac. *Portugal berries.*

(*b.*) The filtrate changes to bottle-green, or reddish-green. *Natural wines, whortleberries, hollyhock, privet, both elders, fuchsine.* Pass to O.

O. Treat 2 cc. of the clarified wine with 3 or 4 cc. of a saturated solution of borax, according to the intensity of the colour of the wine.

(*a.*) The liquid remains wine lilac, or with some violet tinge, *both elders, privet, whortleberries.* Pass to P.

(*b.*) The fluid becomes bluish-grey-flax-blossom, greenish or bluish-grey, with very faint trace of lilac, *pure wine, whortleberries, hollyhock, fuchsine.* Pass to R.

P. Treat a new portion of wine with sodium bicarbonate (as directed at I.).

(*a.*) The tint, at first lilac, changes afterwards to grey, slightly brownish, or to maroon. If a new portion be treated with sodium carbonate, according to C., and then heated to boiling, it becomes clearer, and loses its green tint.

The lake obtained according to E. is deep blue-green. DWARF ELDER.

(*b.*) The specimen remains grey, tinged with green, bottle-green, or yellowish. Sometimes (black elder) it acquires a lilac tint, which almost immediately disappears, changing to a greenish-grey-blue, *whortleberries, black elder, privet.* Pass to Q.

Q. Treat a specimen of the wine with alum and carbonate of soda (as directed at E.). Shake the mixture, and after a few moments throw it on a filter.

(*a.*) The lake remaining on the filter is deep green-blue; the filtrate is clear bottle-green. A sample treated with sodium carbonate (as at C.) darkens and becomes grey, slightly greenish, on heating to boiling. BLACK ELDER.

(*b.*) The lake is clear bluish or greenish. The filtrate is clear bottle-green. A sample treated with sodium carbonate (as at C.), and heated to boiling, changes to dirty yellowish. PRIVET.

(*c.*) The lake is ash-green faintly rose-tinted. The filtrate is bottle-green, with tint of maroon. A sample treated with sodium carbonate (according to C.) becomes deep grey on being heated to boiling. WHORTLEBERRIES.

R. Treat a specimen of the wine with ammonia and ether, as directed at J.

(*a.*) The ether being decanted and evaporated, the fluid residue becomes rose-coloured on treatment with acetic acid. FUCHSINE.

(*b.*) The liquid left after the evaporation of the ether does not become red on acidification with acetic acid, *natural wines, hollyhock, whortleberries.* Pass to S.

S. A sample is treated with its own bulk of a solution of aluminium acetate of 2° B.

(*a.*) The colour of mixture remains winey, ***natural wines, whortleberries***; differentiate between them, as directed at L (*a*), and L (*c*).

(*b.*) The colour of the mixture becomes violet-blue, ***hollyhock, whortleberries.*** Pass to T.

T. A specimen is treated with alum, and sodium carbonate (as at E.), and after a few moments filtered.

(*a.*) The lake is clear green, slightly bluish, and rose-tinted; filtrate is bottle-green, with little maroon. With borax (as at O), particularly if the sample has been concentrated, the liquid is grey with trace of lilac. 2 cc. of the liquid treated with 3 cc. of dilute ammonia (1 vol. of liq. ammonia with 10 vols. of water), and the mixture diluted with its own bulk of water, gives a liquid which is yellowish-grey, greenish or greenish-grey. The other characteristics as at L. WHORTLEBERRIES.

(*b.*) The lake is green, slightly bluish, quite free from rose, filtrate clear bottle-green. With borax the liquid is greenish blue-grey. With ammonia (as above), dark bottle-green. With aluminium acetate (as at S.), bluish-violet coloration. HOLLYHOCK.

Although somewhat difficult, this systematic method serves for the discovery of several colouring-matters mixed in one wine, if the indications of Tables A. and B. are carefully observed and followed. It is always desirable to determine the presence of fuchsine by the special reactions given further on. By means of Table B. the presence of one or several of the colouring-matters may be detected; but before deciding, it is as well to verify by repeating, for the substances so found, the reactions of Table A. on the sample; and also the more special characteristics given further on, for the identification of those substances.

SPECIAL REACTIONS FOR THE DETECTION OF CERTAIN OF THE COLOURING-MATTERS MIXED WITH WINES.

Brazil Wood.—Even a very strong clarification (two or three times more albumen than mentioned at the head of Table B.) does not wholly decolourise the adulterated wine. It becomes yellow-buff, which on exposure to the air gradually changes to red. If a wine that has been adulterated with Brazil-wood is clarified, and then a skein of scoured silk, washed with dilute tartaric acid, be soaked in it for twenty-four hours, and then withdrawn, washed, and dried at 60° to 70°, the silk will be found to be dyed lilac-maroon, or red. In pure wine, the skein remains wine-coloured or lilac.

If the dyed silk be now dipped into dilute ammonia, and heated to 100° for a moment, it becomes lilac-red, if Brazil-wood were present; but deep grey, with scarcely a tinge of its original colour, if the wine were pure. If the ammonia be replaced by lime-water, the skein changes to ash-grey if Brazil-wood were present; but to a dark, dirty-yellowish-red, if the wine were pure. Finally, if the skein be dipped into aluminium acetate, and then heated to 100°, it retains its wine-red lilac colour. This reaction differentiates Brazil-wood from logwood.

Logwood.—If the colour due to logwood is in excess in the wine, ammonia gives it a shade of violet; if the proportion of logwood is small, the reactions B, L, N, of Table A., which are very delicate, should be tried.

A skein of silk, prepared in the manner described for Brazil-wood, and treated with logwood, becomes dyed lilac-red, or maroon, which dilute ammonia changes to violet-blue tinged with grey, and which by acetate of aluminium becomes bluish-violet.

Cochineal.—The lilac, or roseate tints due to the reactions A, B, H, K, of Table A., are very sensitive, the last being very characteristic; the only substance likely to be confounded with it is the phytolacca (Portugal berries), which is differentiated by the reaction B, of the same table.

A skein of scoured silk, mordanted with aluminium acetate soaked in the clarified wine for twenty hours is dyed of a wine violet colour, analogous to that of pure wine, on being dried at 100°. The colour does not change, even at 100°, by cupric acetate (exclusion of fuchsine); but if the skein be dipped into a dilute solution of zinc chloride, heated to 100°, and then wetted with sodium carbonate, washed with water and dried, the colour becomes fine purple, whereas with pure wine the tint would remain sombre grey-lilac.

Cochineal may be discovered by the spectroscope if present in large quantity, but if it amounts to only about 12 per cent. of the total coloration, it cannot be so detected. It rapidly separates from wines, being precipitated in the lees.

Fuchsine.—This should be sought for in all wines found to be adulterated with other substances. The reaction J of Table B., p. 456, is very sensitive. Great care must be taken to avoid loss of rosaniline from imperfect decomposition of its salts in solution; moreover, arsenic should always be sought for where the wine is found to contain any aniline. Fuchsine rapidly separates from the wines to which it has been added. A skein of silk becomes dyed rose by soaking in a wine adulterated with fuchsine, and its colour passes to yellow on treatment with hydrochloric acid, but to bright red if the wine was pure. The dyed skein

treated with dilute cupric acetate, and dried at 100°, becomes fine deep rose-violet if fuchsine is present, and of a lilac tinged with ash-grey if the wine is pure. This reaction is very sensitive.

Phytolacca.—(Portugal berries). The rose or lilac colorations of the reactions A, G, and especially C of Table A., are very sensitive.

Hollyhock—(*Althea rosea*), much used. This substance imparts a peculiar flavour, which in a few months becomes actually disagreeable, while the colouring-matter itself rapidly precipitates.

Beetroot.—This is generally employed only to mask other adulterants. The lilac tint of reaction C of Table A., if the beetroot is fresh, and the yellowish colours due to alkalies (reactions D, E and F of Table A.) are very sensitive, even with old decoctions.

Black Elder, Dwarf Elder.—The dwarf elder imparts a faint turpentine odour to the wines. The berries of both varieties are particularly used to communicate a special colour and flavour to port wine. The *teinte de Fismes*, which is largely used at Fismes, Paris, and elsewhere, is made by digesting 250 to 500 parts of elder-berries, and 30 to 60 parts of alum, with 800 to 600 parts of water, and then submitting the mixture to pressure. M. Maumené reports having discovered as much as 4 to 7 grms. of alum per litre in wines adulterated with this substance. Sometimes (though rarely) the alum is replaced by tartaric acid. Wines adulterated with either yield a violet-blue lake (reaction H, Table A). By comparison with pure wine the difference is very marked.

A piece of flannel, or skein of silk, mordanted with aluminium acetate, heated for some time in the suspected wine, then washed, and immersed in water made faintly alkaline with ammonia, becomes green if the wine is pure, but dark brown if black elder is present. Probably the same reaction occurs with dwarf elder.

Privet.—This is very seldom used. The general reactions, particularly N and P of Table A., must be relied on.

Myrtille—(Whortleberries). Very seldom used, and only for the commonest wines. The principal characteristics are given in L (*c*), Table B., p. 467. In wines suspected to be adulterated with this substance, citric acid should be sought for, its presence being one of the best indications of the adulteration.

Indigo.—The reactions A (*b*) and B (*b*) of Table B., p. 464, are so sensitive that they are alone sufficient to characterise indigo. Wool or silk mordanted with aluminium acetate, heated with 20 to 40 cc. of the suspected wine nearly to dryness, washed and

then dipped into very dilute ammonia, become dirty green if the wine be pure, but blue if indigo be present.

Indigo being often used to mask the too bright colours of cochineal and fuchsine, these should always be sought for after the removal of the indigo by clarification with albumen.

Indigo very rapidly separates from wines, and it may frequently be found in the lees, even when the wine itself gives no indication of its presence.

Substances other than those mentioned are occasionally employed for the adulteration of wines; among them are archil residues, sulpho-purpuric, and sulpho-alizaric acids, and their salts; but these have only recently been introduced, and are not yet seriously employed. Except in such cases as indigo and cochineal, it is only upon a series of concordant reactions that the presence of an artificial colouring-matter should be affirmed.

§ 285. *Mineral Substances, or Ash.*—The ash of a great many wines, and especially of sherries, imported into this country, consists nearly entirely of sulphates.* This is due either to sulphuring or plastering. It is sometimes found absolutely necessary to charge a wine slightly with sulphurous acid, which in course of time becomes sulphuric acid; and in such a case the chlorides and carbonic acids are diminished in the ash, and the sulphuric increased, but the total weight of the ash itself is not materially increased. On the other hand, plastering (by which is meant the addition of plaster of Paris to the grapes before they are crushed) has the effect, by its reaction on cream of tartar, of producing a soluble sulphate of potassium, which may very materially increase the ash of the wine.

Under absolutely normal conditions, the ash consists of carbonate, sulphate, phosphate, chloride of potassium, chloride of sodium, phosphate and carbonate of calcium, with very small quantities of magnesia, iron, silica, and frequently lithium and manganese.

The ash from a litre of wine examined by Boussingault contained—

	Grms.
Potash,	0·842
Lime,	0·092
Magnesia,	0·172
Phosphoric Acid,	0·412
Sulphuric Acid,	0·096
Chlorine,	a trace
Carbonic Acid,	0·250
Sand and Silica,	0·006
	1·870

* The sulphuric acid in sherries ranges from 1·5 to 8 grms. per litre (equal to 19·0 to 93·3 grains per bottle of ⅙ gallon).

With regard to the analysis of the ash, &c., see p. 98 *et seq.*

§ 286. *Prosecution as to Unfermented Wine.*—In March, 1880, a case was heard at the Salford police court in which a chemist and druggist was summoned for selling a bottle of "unfermented port wine," and also a bottle of "unfermented sherry wine," which were not of the nature, substance, and quality of the article demanded. The port wine was labelled . . . "unfermented port wine, manufactured from the juice of the grape for sacramental and other purposes." There was a similar label on the sherry bottle. The analysis by Mr. Carter Bell of these samples was as follows:—

	Port.	Sherry.
Specific gravity, .	1100	1098
Volatile acid calculated as acetic, . .	·006	·006
Tartaric acid, . .	·502	·581
Sugar (invert), . .	21·2	22·9
Ash, ...	·0395	·019
Insoluble ash in water,	·0185 or 46·8 per cent.	·009 or 47·3 per cent.
Soluble ash, . .	·0210 or 53·1 per cent.	·010 or 52·6 per cent.
Residue dried at 230°,	24·50	25·421
Salicylic acid, . .	·02	·10

The analyst stated that in the wines he found no trace of the juice of the grape.

The pure juice of the grape in 1000 parts contained three of ash, and that ash should mainly consist of potash, phosphoric acid, and other elements. About 90 per cent. of such an ash should be soluble in water. In the sherry wine he had only found ·190 per thousand of ash, which was considerably less than one-tenth of what ought to be found in pure grape juice (see p. 438). This ash contained a trace of potash and a trace of phosphoric acid. It consisted chiefly of sulphate of sodium and calcium, and a few other ingredients. 52 per cent. of it only was soluble in water. It was no greater in quantity than could be obtained from ordinary drinking water. He considered that the so-called sherry was nothing more than a solution of sugar and tartaric acid flavoured and coloured, and containing a little salicylic acid. He gave very similar evidence with regard to the port. On cross-examination, he could not swear that there was not some percentage of the juice of the grape in it. For the defence it was contended that when sold there was not the slightest deception; the inspector did not ask for pure juice of the grape, and did not get it; but he asked for unfermented wine manufactured from the juice of the grape and got it. Witnesses were called who swore that the wine was made from grape juice, the manager stating, with some reluctance, that he generally put one part of grape juice to five parts of water; to six gallons of this liquid was added two pounds of sugar. The stipendiary magistrate dismissed the case on the ground that there was no standard of what amount of grape juice the wine should contain, and there was evidence to show that it did contain some grape juice, and therefore, it could not be said that the manufacturers had made the wine fraudulently from water.—*Analyst*, 1880, p. 110, and 1881, p. 197.

BIBLIOGRAPHY.

BATILLIAT.—"Traité sur les vins de la France."
BERTHELOT et DE FLEURIEN.—*Journ. Chim. Méd.* [3], 1864, t. xlvi., p. 92.

CAMERON, C. A.—*Analyst*, i., 1877, p. 99.
CHANCEL, G.—*Comptes Rendus*, lxxxiv. 348–351.
CHEVALLIER.—*Ann. d'Hyg.*, 1856, t. v.; 1857, t. vij.; 1870, t. xxiii.; 1876, t. ij., &c.
DUCLEAUX, E.—*Ann. Chim. Phys.* [5], ij., p. 233–289.
DUPRÉ, A.—*Proceedings of Soc. of Analysts*, i., 1876; *Analyst*, i., 1877, 26, 186.
GAUTIER.—*Bull. Soc. Chim.* [2], xxv.
GRIFFIN, J. J.—"The Chemical Testing of Wines and Spirits." London, 1872.
HAGER.—*Pharm. Central Halle*, 1872, No. 27.
HASSALL.—"Food and Air," 1874.
JACQUEMIN.—*Bull. Soc. Chim.* [2], xxvj., 68–71; *Analyst*, i., 1877, 148.
LASSAIGNE.—*Journ. Pharm. et Chim.*, 4e sér., 1870, t. xi.; *Ann. d'Hyg.* [2], 1831.
MAUMENÉ, E. J.—"Traité théorique et pratique du travail des vins." 2e éd., Paris, 1874.
ODEPH, ALP.—*Journ. Chim. Méd.*, 4e sér., 1860, t. vj.
NEUBAUER, C.—"Ueber die Chemie des Weines." Wiesbaden, 1879.
PASTEUR.—"Nouvelles observations sur la conservation des vins." 8vo, Paris, 1868.
POGGIALE.—*Journ. Pharm. et Chim.* [3], 1859, t. xxxvj., p. 164.
THUDICHUM, J. L. W., and DUPRÉ, A.—"A Treatise on the Origin, Nature, and Varieties of Wine." 8vo, London, 1872.
VOGEL, H. W.—*Deut. Chem. Ges. Ber.*, ix., 1900–1911.

PART VII.

VINEGAR.

§ 287. *Constituents of Commercial Vinegar.*—Commercial vinegar is a more or less impure acetic acid, containing usually acetic acid, acetic ether, alcohol, sugar, gum, extractive matter, alkaline acetates and tartrates, a variable amount of salts (depending on the substances from which it has been produced), and legally not more than one-thousandth of its weight of pure sulphuric acid.

Varieties of Vinegar.—The chief varieties of vinegar are as follows:—

(1.) *Malt-Vinegar.*—The great majority of commercial vinegars in this country is derived from the acetous fermentation of a wort, made from mixtures of malt and barley. Malt-vinegar is of a decided brown colour, in specific gravity varying from 1·017 to 1·019; it is of various degrees of strength, the manufacturers distinguishing different kinds as Nos. 18, 20, 22, and 24 respectively, the last being the strongest, and containing about 4·6 per cent. of acetic acid. That made by one of the largest firms in this country will be found to contain from ·1 to ·16 per cent. of combined sulphuric acid, and from ·04 to ·08 per cent. of chlorine, as chlorides.

(2.) *Wine-Vinegar* is the chief vinegar in Continental commerce. It is prepared from grape-juice and inferior new wines; that made from white wine is most esteemed. The wine-vinegars vary in colour from pale yellow to red; they have nearly always an alcoholic odour; specific gravity from 1·014 to 1·022. A litre of Orleans vinegar (according to Chevallier's* analyses of actual samples) saturates from 6 to 7 grms. of dry carbonate of soda. The extract from pure wine-vinegar varies from 1·7 to 2·4 per cent., the average being 2·05 per cent., and usually contains ·25 grm. of tartrate of potash.

Vinegars of limited use are—*Glucose-vinegar*, recognised chiefly by the presence of dextrine, which may be precipitated by alcohol; *beer-vinegar*, from sour ale; *cider-vinegar*, made both from apples and pears; *crab-vinegar*, made from the crab apple, and

* *Journ. d'Hyg.*, 1877, No. 45.

used nearly all over Wales and Monmouthshire; and various artificial vinegars.

§ 288. *Adulterations.*—The adulterations of vinegar are—

(1.) Water.

(2.) Mineral acids, especially sulphuric, more rarely hydrochloric, and still more rarely nitric acids.

(3.) Metallic adulterations, or rather impurities; such as arsenic,* derived from sulphuric acid, copper,† lead, zinc, and tin, from the solvent action of the acid on any metallic surfaces with which it may have come in contact.

(4.) Pyroligneous acid.

(5.) Various organic substances, such as colouring agents, and capsicum.

§ 289. *Analysis of Vinegar*—(1.) *Water.*—Vinegar should contain at least 3 per cent. of acetic acid, and if it does not do so, it may be safely returned as adulterated with water; for it then is so dilute as certainly not to be of the nature and quality of the substance usually sold as vinegar. The strength of vinegar may be accurately estimated by distilling 110 cc., until 100 cc. have been drawn over, that is, ten-elevenths. The 100 cc. will contain 80 per cent. of the whole acetic acid present in the 110 cc., and may be titrated; or the specific gravity of the distillate may be taken, and the strength found from the following table:—

Per cent.	Specific Gravity.
1	1·001
2	1·002
3	1·004
4	1·005
5	1·007
6	1·008
7	1·010
8	1·012
9	1·013
10	1·015
11	1·016

* "The observation of M. Deschamps induced us to analyse a vinegar sold by a certain Sieur C. . . . The presence of arsenic in this vinegar was ascertained, and the Sieur C. was compelled to confess that the vinegar had been mixed with wood-vinegar. On resorting to the person who furnished the latter product, the whole of the wood-vinegar in his possession was found arsenical, and seized, in order to be employed only for industrial use."—"Le Vinaigre," Chevallier, *Journ. d'Hyg.*, No. 46, June, 1877.

† Seven out of twelve samples of vinegar sold in Paris, and analysed by Alfred Riche, contained copper varying from 5 to 15 mgrms. per litre. *Journ. Pharm. Chim.* [4], xxvj. 23–28.

Per cent.	Specific Gravity.
12	1·017
13	1·018
14	1·020
15	1·022
16	1·023
17	1·024
18	1·025
19	1·026
20	1·027

Vinegar may also be distilled in a vacuum produced by the mercury pump described at p. 70; it should be distilled into caustic soda or potash of known strength, and then titrated back. By distilling thrice to dryness, adding a little water each time, the whole of the acetic acid comes over.

It will be necessary to test the distillate for the presence of hydrochloric acid, and also to take the acidity of the vinegar without distillation, so as to control the results.

The titration of vinegar may be made with ordinary soda solution, and approximate results obtained.* If absolutely accurate determinations are required, it is best to add an excess of carefully weighed pure carbonate of lime to a known weight of the vinegar; the liquid is boiled, filtered, and the residual carbonate of lime filtered off, dissolved in slight excess of normal hydrochloric acid, and titrated back with caustic soda and cochineal solution. From the amount of carbonate thus found to have been unacted on by the vinegar, the total acidity is calculated.

(2.) *Mineral Acids.*—A great many commercial vinegars contain no trace of free mineral acid; and it has been amply shown that although one-thousandth part of free sulphuric acid is allowed by law, such addition is not by any means necessary for the preservation of the vinegar. The mineral acid, if present, is nearly always sulphuric, occasionally hydrochloric, and still more rarely nitric acid.

Hydrochloric Acid is detected by the distillation already described, and the testing of the distillate with nitrate of silver.

Nitric Acid may (in the absence of other reducing agents) be detected by the rapid decoloration of a solution of indigo carmine added to the boiling vinegar.

Sulphuric Acid cannot be detected by the usual chloride of barium test, for it fails to distinguish between free and combined sulphuric acid. The charring effect of the acid on paper, on

* The results are only approximate, because sodic acetate has itself a feeble alkaline reaction.

sugar, or its action on starch (formerly taken as the basis of the older tests), is now replaced by more scientific methods, and need not be described here.

One of the most speedy tests for the presence of mineral acids is that proposed by A. Hilger*:—Two or three drops of a solution of methyl aniline violet (0·1 : 100) are added to 25 cc. of vinegar; if pure, no colour is produced; but if ·2 per cent. of any mineral acid is present, the colour is blue; or if ·5 per cent., blue-green; and if 1 per cent., green.

Another useful test is that of M. Strohl;† it is based on the well-known fact, that oxalate of lime is insoluble in acetic, but soluble in mineral acids.‡ The solutions requisite are—a solution of calcic chloride (15·1 grms. to the litre) and a solution of crystallised ammonic oxalate (28·4 grms. to the litre); ½ cc. of each of these liquids is added to 50 cc. of the vinegar under examination, and if the turbidity which is at first produced does not disappear, the liquid contains less than—

1·70	grm. per cent.	sulphuric acid	(specific gravity	1·843)	per litre.
2·85	,,	hydrochloric acid	(,, ,,	1·174)	,,
4·40	,,	nitric acid	(,, ,,	1·174)	,,

The test, without claim to great accuracy, is extremely useful; for if any suspicious indication be observed, the vinegar may be then submitted to a more elaborate examination for free acids.

As speedy as any of the foregoing, and at once more scientific and accurate, is the process introduced by Mr. Hehner. Its principle is based upon the fact that vinegar always contains potash and soda salts of the organic acid; hence, it is obvious that sulphuric or hydrochloric acids, if added in small quantity, merely decompose an equivalent quantity of acetate or tartrate, as the case may be, and *as free acids* immediately disappear; but if added in excess of the amount of acetates and tartrates, the excess remains as free acid. It thus follows, that if any undecomposed acetate or tartrate exists in the vinegar, it is impossible for a free mineral acid to be present; and since the acetates and tartrates are decomposed by ignition into carbonates, the readiest way to ascertain their existence is to examine the ash of the vinegar for carbonates. If that ash is *neutral*, free mineral acid is probably present; if *alkaline*, no free acid can be present, although, of course, a small quantity may originally have been added.

The qualitative test devised by Mr. Hehner is also made

* *Archiv. der Pharmacie*, 1876, 193.
† *Arch. Pharm.* [5], 4, 342-346.
‡ *Ibid.*

quantitative. If an accurately-estimated volume of d. n. soda solution is added to a known quantity of the vinegar, so as to neutralise slightly in excess the total amount of free mineral acid present, on ignition the alkalinity of the ash gives the measure of the quantity of free sulphuric or hydrochloric acid. The exact details of this operation, as practised by Mr. Hehner, are as follows:—50 cc. of the vinegar are mixed with 25 cc. of d. n. soda; the liquid is evaporated on a water-bath in a platinum basin, the residue dried at about 110°., and carefully incinerated at the lowest possible temperature—the ash need not be burned white. 25 cc. of a d. n. sulphuric acid solution are now added to the ash, the liquid heated to expel free CO_2, and filtered. The filter is washed with hot water, litmus added,* and the acidity ascertained by d. n. soda. The volume of soda necessary for neutralisation directly gives the proportion of free mineral acid present in the vinegar, 100 cc. of d. n. corresponding to ·49 grm. of H_2SO_4. If the amount of alkali originally added should have been insufficient, it is necessary to recommence the experiment. For this reason Messrs. Allen and Bodmer made some experiments in which the preceding manipulation was modified by neutralising the *whole* of the acid, organic and inorganic, by soda solution. The results were satisfactory, but great care must be taken to titrate accurately.

Another very satisfactory way of separating and identifying the free mineral acids in vinegar is the following:—Saturate a known quantity with quinine, evaporate to dryness, take up the quinine salts with spirit, recover the spirit by distillation, dissolve the quinine salt in water, and precipitate by ammonia. The aqueous liquid will now contain the acetate of ammonia, together with the sulphate, chloride or nitrate; if any one, or all three, of the free acids were present, the acids may be determined in the usual way.

A method of separating free sulphuric acid from sulphates is to evaporate the vinegar to a syrup, precipitate the sulphates by alcohol, filter, wash the precipitated salts with alcohol, and determine the free sulphuric acid in the alcoholic solution. Provided sufficient alcohol be added, the separation of free from combined sulphuric acid is exact.

Another method, the principle of which was proposed by Mr. Thresh, and which has been improved upon by Mr. W. C. Young, is to add to a known measure of vinegar an excess of $BaCl_2$; the chlorine in a portion of the liquid is now determined with great care, the rest is evaporated, ignited, and the chlorine of the ash

* Instead of litmus, cochineal may be used; the latter is unaffected by CO_2, and therefore preferable.

determined. The difference represents the free mineral acid in terms of chlorine. The presence of free tartaric or citric acids quite invalidates the accuracy of the process, but, with these exceptions, it is generally applicable.

(3.) *Metallic Adulterations.*—Metals in vinegar are detected by saturating the liquid with hydric sulphide, or by specially testing for arsenic, copper, zinc, tin, and lead, by the methods detailed in the second volume of this work. Metals of the first group may, however, be presumed absent, if there is no deepening of colour on saturation with hydric sulphide; arsenic, if Reinsch's test gives negative results; and zinc, if the nearly neutralised vinegar gives no precipitate with hydric sulphide.

(4.) *Pyroligneous Acid.*—The addition of pyroligneous acid to vinegar is said to be revealed by the presence of an excess of sulphate and acetate of soda.

(5.) *Organic Adulterations.*—The other organic adulterations—such as capsicum—must be looked for in the extract; Chevallier has found fuchsine in French vinegars. Methods for the detection of this in wine, given at p. 470, &c., are also applicable to vinegar.

BIBLIOGRAPHY.

Allen, A. H., and Bodmer, R.—Experiments on the Determination of Free Acids in Vinegar. *Analyst*, iii., 1878, 268.

Boettger.—*Journ. Pharm. et Chim.* [3], 1845, t. viij., p. 113.

Cauvet.—Examen et analyse des vinaigres. *Ann. d'Hyg. et de Méd Lég.*, 2e série, 1874, t. xli.

Chevallier, Gobley, et Journell.—Essais sur le vinaigre, ses falsifications, les moyens de les reconnaître, &c. *Ib.*, 1843, t. xxix., p. 55.

Chevallier.—*Ib.*, 1839, t. xxi., p. 86. *Journ. d'Hyg.*, 1877, No. 45.

Gaultier de Claubry.—*Ib.*, 1841, t. xxvij.

Guibourt.—*Journ. Pharm. et Chim.* [3], 1846, t. x., p. 91.

Hehner, O.—Sulphuric and Hydrochloric Acids in Vinegar. *Analyst*, i., 1877, p. 105.

Pasteur.—"Études sur le vinaigre." Paris, 8vo, 1868.

Thresh, J. C.—*Pharm. Journ.*, July 3, 1875.

Young, W. C.—On Sulphuric Acid in Vinegar. *Analyst*, ii., 1878, 163, 203.

LEMON JUICE AND LIME JUICE.

§ 290. Lemon juice is the expressed juice of the *Citrus limonum*, and lime juice that of the *Citrus acida* and *Citrus limetta*. The Board of Trade standard for lemon juice is a density of 1·030 [when dealcoholised], and an acidity equivalent to 30 grains per ounce

of citric acid. The British pharmacopœia directs that lemon juice should have a specific gravity of 1·039, and should contain 32·5 grains of citric acid per ounce.

Lemon, lime, and bergamot juice are all similar in their composition, containing citric acid as the predominant free acid, and small quantities of acetic, formic, and other organic acids, together with albumen, sugar, mucilage, and extractive matters. The mineral matter is very small, and contains 54 per cent. of its weight in potash and 15 per cent. of phosphoric acid.

The juice is expressed in England, and also in Sicily, where the method of preparation is to mix one ounce of brandy with ten ounces of the juice, and over the surface of the liquid to pour a layer of olive oil. This crude process of preservation is effectual, but is now being supplanted by more modern methods.

The following table shows the specific gravity, free acid, and combined organic acid, the acid being expressed in terms of crystallised citric acid, of the citric commercial juices [*Allen*]:—

	Specific Gravity.	Free Acid. Ozs. per gallon.	Combined Organic Acid. Per gallon.
Lemon Juice—			
Raw Sicilian, .	...	6 to 9	0·85
,, English, .	1·04 to 1·05	11 to 13	0·3
Concentrated, .	1·20 to 1·25	57 to 72	6 to 8
Bergamot Juice—			
Concentrated, .	1·22 to 1·25	47 to 55	7 to 8
Lime Juice—			
Raw, . . .	1·035 to 1·040	10·6 to 13·5	0·4 to 0·7
Concentrated, .	1·28 to 1·38	82 to 112	8·6

§ 291. *Adulterations and Analysis of Citric Juices.*—Lime juice has been rather extensively adulterated, and at the present time it is by no means uncommon to meet with a wholly fictitious article under this name.

Sulphuric, hydrochloric, and nitric acids are the main foreign ingredients to be sought for. The general principles of the detection of these acids in a free state are entirely the same as in vinegar, and the remarks with regard to the alkalinity of vinegar-ash when genuine apply equally to the ash from the citric juices. (See p. 478.) Good juice contains insignificant traces of sulphates and chlorides, so that the mere addition of silver nitrate or of barium chloride will at once show whether there has been any tampering with the liquid.

Nitric acid may be detected by the ordinary tests for that acid. The juice may be boiled with metallic copper, when red fumes will appear, should nitric acid be present. Or, it may be much diluted and filtered, and one portion be made neutral with burnt magnesia, and boiled to expel all free ammonia; afterwards, by acting upon the liquid with a copper zinc couple, any nitrates may be turned into ammonia, distilled over, and titrated in the usual way.

F. Scribani* adds to the suspected lemon juice an aqueous solution of ferrous chloride, strongly acidified with hydrochloric acid and free from ferric salt. The liquid is boiled for a few minutes, and then a little sulphocyanide is added. If nitric acid has been present, it will have oxidised the ferrous salt into a ferric salt, and a deep blood-red colour will be produced by the test.

§ 292. *The Analysis of Lime Juice*, with a view to ascertain its strength, is confined to the determination of the amount of citric acid and citrates.

The amount of citric acid is determined frequently for technical purposes by the aid of a special hydrometer, called "a citrometer," but this method is not exact enough for the purposes of the food-analyst. Nevertheless, it will always be well to take the specific gravity of the juice by a specific gravity bottle, or by the methods detailed at page 71, first boiling off any alcohol which the juice may contain, and making it up to the same bulk as before the dealcoholisation.

The amount of free acid may be estimated by means of decinormal soda. A known quantity of the juice is taken and coloured with phenol-phthalein, and then d. n. soda is run in until the colour changes. About 10 cc. of the ordinary raw juice may be taken and diluted to 50 cc.; but the concentrated juice must be much diluted before titration.

The free acid known, the next step is to determine the amount of citrates and other organic acids combined with bases. For this purpose, the measured quantity of the juice which has already been neutralised by soda, is evaporated down, charred, and the charred mass treated with a known volume of decinormal sulphuric acid, which must be sufficient to more than neutralise the carbonates.

The acid solution is filtered and neutralised by d. n. soda; this will give the necessary data from which to calculate the amount of sulphuric acid used by the carbonates produced by the action of heat on the organic acids. This amount is equi-

* *Gaz. Chim. Ital.*, viii. 294.

valent to the total amount of organic acid; if expressed as citric acid, forty-nine parts of sulphuric are equal to seventy of $H_2C_6H_5O_7H_2O$, or sixty-seven of $2H_3C_6H_5O_7H_2O$.

The amount of free acid already obtained is now subtracted from the total acid, the difference being that which is combined with bases.

To ascertain the amount of real citric acid present in the juice, it must be determined as citrate of lime, for it need hardly be said that the process given above does not distinguish between malates, meconates, or any other organic acids converted by heat into carbonates. To determine the real citric acid, Mr. Warrington* recommends the following processes: from 15 to 20 cc. of raw lime juice are exactly neutralised by d. n. soda, the whole made up to about 50 cc., and heated to boiling.

While boiling, so much of a solution of chloride of lime is added as is known to be rather more than equivalent to the total amount of organic acids present. The boiling must be continued for half an hour, and the precipitate collected and washed with hot water. The filtrate and washings are evaporated to a small bulk (not more than 15 cc.), and a little ammonia added to exact neutralisation, if the liquid gives an acid reaction; a further precipitation takes place, and this second precipitate must be collected on a filter. The filters are dried and burnt up at a low heat, and their neutralising power with regard to acid is determined. For this purpose, the ash may be dissolved in standard hydrochloric acid, and titrated back; each cc. of normal HCl neutralised is equivalent to ·070 grm. of crystallised citric acid. If either oxalic or tartaric acids should be present, the results are, of course, inaccurate.

* *Journ. Chem. Soc.*, 1875, 934.

PART VIII.—CONDIMENTS: MUSTARD, PEPPER, &c.

MUSTARD.

§ 293. *Mustard* is made from the seeds, finely ground, of the *Sinapis nigra*, or black mustard, or from those of the *Sinapis alba*, or white mustard, or again, from a mixture of both varieties. The manufacturer reduces the seeds to powder, and passes the product through a series of sieves. The portion in the first sieve is called the *dressings*, that which passes through is an impure *mustard flour*. The impure flour, on being passed through a second sieve, yields the pure flour of mustard and a second quantity of dressings. The dressings are utilised, by being submitted to pressure, for the sake of the fixed oil they contain.

Microscopical Structure of the Seed.—The white mustard seed is made up of the husk and the seed proper. The *seed proper* is simple in structure, consisting entirely of minute oil-bearing cells; their size averages ·00041 inch in the finely powdered seed; and they look extremely like starch corpuscles, but neither polarise light nor strike a blue colour with iodine.

The *husk* is more complex, and consists of three membranes:—

1. An outer membrane, composed of two kinds of large transparent cells, which are described by Dr. Hassall thus:—Those of the first kind are of an hexagonal figure, and united by their edges so as to form a distinct membrane, the centre of each cell being perforated; the cells of the second kind occupy the apertures which exist in the previously-described cells, and they are themselves traversed by a somewhat funnel-shaped tube, which appears to terminate on the surface of the seed. Immersed in water, these cells swell up to several times their original volume, occasion the rupture of the hexagonal cells, and become themselves much wrinkled or corrugated, the extremity of the tubes in some cases being seen protruding from the proximate termination of the cells. It is possible, however, that what are here described as two different kinds of cells really form distinct parts of the same cells. It is from these cells that the thick mucilage obtained by digesting mustard seeds in water is derived.

TABLE L.

	White Mustard.					Brown Mustard.			
	Mustard, whole seeds.		Mustard farina.			Mustard, whole seeds.	Mustard farina.		
	Yorkshire.	Cambridge.	Superfine.	Fine.	Second.	Cambridge.	Superfine.	Fine.	Second.
Moisture,	9·32	8·00	6·30	5·78	6·06	8·52	4·35	4·52	5·63
Fat,	25·56	27·51	37·18	35·74	32·55	25·54	36·96	38·02	36·19
Cellulose,	10·52	8·87	3·90	4·15	9·34	9·01	3·09	2·06	3·26
Sulphur,	0·99	0·93	1·33	1·22	1·26	1·28	1 50	1·48	1·30
Nitrogen,	4·54	4·49	5·05	4·89	4·25	4·38	4·94	5·01	4·31
Albuminoids,	28·37	28·06	31·56	30·56	26·56	26·50	29·81	30·25	26·06
Myrosin and albumen,	5·24	4·58	7·32	6·67	6·11	5·214	6·46	6·78	6·14
Soluble matter,	27·38	26·29	36·31	36·60	33·90	24·22	31·14	32·78	31·41
Volatile oil,	0·06	0·08	0·03	0·04	0·03	·0473	1·437	1·500	1·381
Potassium myronate,	...	...	...	...	...	1·692	5·141	5·366	4·940
Ash,	4·57	4·70	4·22	4·31	4·30	4·98	5·04	4·84	4·91
Ash soluble,	0·55	0·75	0·44	0·55	0·33	1·11	1·01	0·98	0·77

2. The second layer, or *middle tissue*, consists of very minute, angular, coloured cells.

3. The inner or third layer of the husk consists of a single layer of angular cells.

The black mustard, in its structural composition, differs from the white only in not containing the large perforated cells of the husk, the outer membranes consisting of two or three layers of large, transparent, hexagonal cells, the other structures being similar to those already described.

§ 294. The accompanying tables (L., LI.) give some careful analyses by C. H. Piesse and Lionel Stansell* of black and white mustard :—

TABLE LI.—ANALYSES OF ASH OF MUSTARD SEED.

	White Seeds.		Brown Seeds.
	Yorkshire.	Cambridge.	Cambridge.
Potash,	21·29	18·88	21·41
Soda,	0·18	0·21	0·35
Lime,	13·46	9·34	13·57
Magnesia,	8·17	10·49	10·04
Iron oxide,	1·18	1·03	1·06
Sulphuric acid,	7·06	7·16	5·56
Chlorine,	0·11	0·12	0·15
Phosphoric acid,	32·74	35·00	37·20
Silica,	1·00	1·12	1·41
Sand,	1·82	1·95	1·38
Charcoal,	12·82	15·14	7·57
	99·85	100·48	99·70

§ 295. *The Chemistry of Mustard* is extremely interesting; both seeds, white and black, contain a fixed oil (from about 36 per cent.), and a sulphocyanate of sinapin and myrosin. Black mustard seeds contain, in addition to the foregoing, myronate of potash (about ·5 to ·6 per cent.) When the powdered black mustard seeds (or the mixed black and white) are moistened with water, the myronate of potash acts upon the myrosin, and produces *the volatile oil of mustard.* White mustard seeds, on the other hand, contain also a sulphur principle, *sinalbin*, not found in black.

Sinapin, $C_{16}H_{23}NO_5$.—Sinapin exists as a sulphocyanate, both

* *Analyst*, 1880, p. 161.

in black and white mustard seeds, as well as in the seeds of *Turritis glabra*, L. It was first prepared by Henry and Garot in 1825. The best process for extraction of the sulphocyanate on a small scale is (according to Von Babo) to exhaust the oil from the seeds by ether, then to treat with cold absolute alcohol, which only takes up a little of the sulphur compound, and lastly, to dissolve the sulphocyanate of sinapin out with alcohol of 90 per cent. The excess of alcohol is then separated by distillation, and the substance crystallises out, yielding about 1·1 per cent.

Sinapin itself cannot be obtained pure, but a watery solution may readily be prepared by decomposing a solution of the bisulphate with a proper quantity of baryta. After filtering away the sulphate of baryta, the filtrate is of a yellow colour and intensely alkaline reaction; it precipitates many metals from their solution, but on evaporation its colour changes through green and red into brown, and at last it leaves behind an uncrystallisable brown residue. On boiling a solution of sinapin with the alkalies or alkaline earths, the sinapin splits up into sinkalin and sinapric acid,

$$C_{16}H_{23}NO_5 + H_2O = C_5H_{13}NO + C_{11}H_{12}O_5,$$

and similar treatment of the sulphocyanate of sinapin produces the same decomposition. To sulphocyanate of sinapin is ascribed the formula $C_{16}H_{23}NO_5CNHS$. It forms colourless, transparent, truncated prisms, in warty or starlike groups, without odour, but of a bitter taste, of neutral reaction, melting at 130° to a yellow fluid, solidifying again in an amorphous mass. Sulphocyanate is readily soluble in water; but ether, turpentine, and bisulphide of carbon do not dissolve it. If to a hot solution in alcohol concentrated sulphuric acid be added, bisulphate of sinapin, $C_{16}H_{23}NO_5$, $SH_2O_4 + 2OH_2$, separates on cooling in rectangular plates. From this salt the neutral sulphate may be obtained by solution in water, and precipitating half the sulphuric acid by baryta.

Sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, a substance which exists only in white mustard, and may be supposed to take the place of myronate of potash. It splits up into sugar, bisulphate of sinapin, and sulphocyanide of acrinyl, C_8H_7NSO. The last, on treatment with alkalies, yields ammonia and the salt of an acid melting at 136°, to which the formula $C_8H_8O_3$ is ascribed.

Myrosin, a substance analogous to emulsin, has not yet been obtained albumen- or lime-free; its solution froths on being shaken; it is coagulated by warming to 60°, as well as by acids and alcohol.

Myronate of Potash, $C_{10}H_{18}KNS_2O_{10}$, crystallises out of spirit, in needles; out of water, in rhombic prisms. It is destitute of water of crystallisation, is of neutral reaction, and has no odour, but is of a bitter taste. It is easily soluble in water, with difficulty in diluted spirit, and scarcely at all in absolute alcohol, whilst it is quite insoluble in ether, chloroform, and benzole. If the concentrated aqueous solution of the salt be digested with tartaric acid and absolute alcohol, the tartrate of potash separated, and the filtered fluid evaporated with carbonate of baryta, the filtrate from the latter will yield easily soluble crystals of myronate of baryta ($C_{10}H_{18}BaNS_2O_{10}$), which soon become opaque on exposure to the air; if heated, it develops ethereal oil of mustard, leaving behind sulphate of baryta. A solution of myronate of potash gives with zinc and hydrochloric acid sulphuretted hydrogen, and then contains a salt of ammonia, sugar, and half of the sulphur as sulphuric acid Boiling hydrochloric acid decomposes similarly. Concentrated potash-lye digested on the dry salt, and heated, develops volatile oil of mustard, cyanide of allyl, and ammonia. If to a watery solution of myronate of potash, myrosin is added, volatile oil of mustard, sugar, and bisulphate of potash are formed; thus,

$$C_{10}H_{18}K.NS_2O_{10} = C_4H_5NS + C_6H_{12}O_6 + SHKO_4,$$

the same reaction takes place if the freshly-prepared watery extract of the white or black mustard seeds be added.

§ 296. *The Fixed Oil of both Black and White Mustard appears to be identical.*—It is a yellow, non-drying oil of 0·915 to 0·920 specific gravity at 15°, solidifying from − 12° to − 16°, and of a mild taste. It contains the glycerides of erucic acid, of stearic acid, and of oleic acid, which last Darby considers different from ordinary oleic acid.

Erucic Acid, $C_{22}H_{42}O_2$, was discovered by Darby in the fatty oil of the seeds of the white and black mustard in 1849, and the same acid has also been found in rape oil. It is easily obtained by saponifying the oil with litharge, treating the soap with ether, which dissolves out the erucate of lead, and decomposing the salt with hydrochloric acid. The erucic acid in solution is filtered from the chloride of lead, the filtrate evaporated in the water-bath, and the residue recrystallised from ether. Erucic acid forms slender, long, white, glittering needles, without odour or taste, melting at from 33° to 34°, and coagulating again at 33°; it is insoluble in water, but dissolves easily in alcohol and ether. The acid, exposed to the air, gradually becomes coloured and rancid. If to water saturated with erucic acid bromine be added gradually, a crystalline compound can be obtained, $C_{22}H_{42}B_2O_2$,

which crystallises out of alcohol in small, white, warty masses, melting at 42° to 43°. Again, if the solution be decomposed with hydrochloric acid and sodium amalgam, it can again be changed back to erucic acid. Erucic acid forms definite salts, of the formula $HC_{22}H_{41}O_2$.

The Volatile Oil of Mustard, C_4H_5NS, is mixed with cyanide of allyl, which may be separated by fractional distillation. Ordinary distillation of black mustard seeds yields it in the proportion of 0·5 to 0·7 per cent. It is colourless or slightly yellow; has a boiling point of 148°, and specific gravity 1009 to 1010; is somewhat soluble in water, dissolving easily in alcohol, ether, and petroleum ether. According to Hager (*Pharm. Centralb.*, x. 65), the commercial oil is much adulterated; he enumerates as fraudulent additions, alcohol, bisulphide of carbon, oil of gilliflowers, and castor-oil. The volatile oil of mustard prevents the coagulation of serum-albumen, as well as alcoholic fermentation. According to Mitscherlich, this is the most deadly of all the ethereal oils, 4 grms. killing a kitten in two hours, 15 grms. in a quarter of an hour. The post-mortem appearances were those of acute gastroenteritis, and the smell of the oil pervaded the blood, urine, and lungs. It has been used in medicine, chiefly externally, for its powerful rubefacient properties, blistering the skin when applied to it.

§ 297. *Adulterations.*—The adulteration most commonly met with is a dilution of ground mustard with turmeric and wheat flour. Other substances usually enumerated as having been fraudulently mixed with mustard are—cayenne pepper, ginger, gamboge, potato starch, pea flour, radish and rape seed, linseed meal, yellow ochre, chromate of potash, plaster of Paris, and clay, besides the ground seeds of the *Sinapis arvensis.*

A careful microscopical examination by both ordinary and polarised light will detect most organic adulterations. If on the addition of iodine to an infusion of the mustard in hot water, no blue colour is produced, it is certain that neither wheat nor any other starch is present.

The chemical examination of mustard, for the purposes of the food-analyst, mainly resolves itself into—

1. Testing for turmeric.
2. Estimation of the total sulphur.
3. Estimation of the fat or oil.
4. Estimation of the ash.
5. Testing for gamboge.

1. *Testing for Turmeric.*—The detection of turmeric by its

microscopical appearance is usually satisfactory; there are, however, some good chemical tests.

A. Extract the mustard with two or three times its volume of methylic alcohol, filter, and evaporate to dryness. If turmeric be present, the addition of hydrochloric acid to the extract will produce a red-orange colour, turned by excess of an alkali to green and blue; or the extract may be dissolved in the least possible quantity of methyl alcohol, and evaporated to dryness in a porcelain capsule, in which there has been placed a small piece of filter paper. When the evaporation is complete, the paper is moistened with a strong solution of boric acid, and then dried; if turmeric be present the paper will take a reddish colour; if it be then treated by an alkali, there is a play of colours, among which green and purple predominate.

B. Advantage may be taken of the fact that the colouring-matter of turmeric is strongly fluorescent; that of mustard, on the other hand, is devoid of fluorescence. The simplest method to detect the fluorescence of the yellow colouring-matter of turmeric, when mixed with mustard, is to pass a little castor-oil through the suspected sample on a filter; the oil, if turmeric be present, shows a very distinct green colour; this is a test of considerable delicacy. Or an alcoholic solution may be placed in a test-tube, and held vertically in water contained in a glass blackened internally; if the observer now slightly incline the top from the window, and look from above *outside* the test-tube, the green fluorescence, if present, will be readily observed.

2. *Estimation of the Total Sulphur.*—Most of the adulterants of mustard contain no sulphur, or at least no very appreciable amount, in the unoxidised state. Mustard, on the other hand, in common with a large number of cruciferous plants, contains sulphur-organic compounds; hence a great deficiency or excess of sulphur is indicative of adulteration, a normal amount no conclusive sign of purity.

The best method to oxidise the sulphur compounds the writer has found to be as follows:—About 1 grm. of the substance is placed in a flask adapted to an upright Liebig's condenser, and digested for some time at a gentle heat with fuming nitric acid. The resulting liquid filters with ease, and the sulphates are precipitated in the usual way with a solution of chloride of barium, the precipitate thoroughly washed, dried, ignited, and weighed; sulphate of bartya multiplied by ·13734 = sulphur. On now making a determination of the sulphates contained in the ash, and subtracting the latter from the former, the amount of *organic sulphur* is obtained.

3. *Estimation of the Fat or Oil.*—This is particularly useful

when wheat starch is the adulterating agent. Wheat flour does not contain more than 1·2 to 2·1 per cent. of oil; mustard, on the other hand, from 33·9 to 36·7 per cent. A weighed portion of the previously dried sample may be placed in the little apparatus figured at p. 68. As a rough guide the following formulæ may be used:—

x Amount of mustard, y of oil found.

$$\frac{33 \cdot 9x}{100} + \frac{1 \cdot 2(100 - x)}{100} = y$$

$$\frac{36 \cdot 7x}{100} + \frac{2(100 - x)}{100} = y$$

4. *Estimation of the Ash.*—The ash is taken in the way already described (see p. 97). The total ash of dried mustard averages 5 per cent. The highest number the writer has obtained is 5·3 per cent., the lowest 5·088 per cent. Of this ash 1·2 at least is soluble in water; in other words, the ash of mustard consists of 30 parts per cent. soluble, 70 parts per cent. insoluble in water. It hence follows, that if found above 5·5 per cent., mineral matters of foreign origin are present; if below 4 per cent., it is an indication of some organic adulterant.

5. *Gamboge.*—Gamboge as an adulterant of mustard is somewhat apocryphal; if suspected of being present, an alcoholic extract of the mustard must be prepared; such an extract when treated with caustic soda becomes of a bright red colour, hydrochloric acid produces a yellow colour.

BIBLIOGRAPHY.

ALLEN, A. H.—*Chem. News*, t. xxvj., p. 84.

BLYTH, A. WYNTER.—"Dict. of Hygiène," Art. Mustard. London, 1876.

BABO u. HIRSCHBRUNN.—*Ann. Chem. Pharm.*, lxxxiv. 10.

BUSSY.—*Journ. Pharm.*, [2], xxvj 39.

DARBY.—*Ann. Chem. Pharm.*, lxix. 1.

HAGER.—*Pharm. Centralb.*, x. 65.

HENRY u. GAROT.—*Journ. Pharm.*, [2], xvij. 1, and xx.

HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.

LUDWIG and LUNGE.—*Zeitsch f. Chem.*, iii. 436, 577.

OTTO, R.—*Ann. Chem. Pharm.*, cxxvij. 183; cxxxv. 226.

PIESSE, CHARLES, and LIONEL STANSELL.—Analyses of Black and White Mustard. *Analyst*, 1880, 161.

STADELER.—*Ann. Chem. Pharm.*, lxxxvij. 133.

WEBSKY.—*Journ. Pract. Chem.*, lviij. 449.

WILL.—*Chem. Centralb.*, 1870, 148.

WILL u. KORNER.—*Ann. Chem. Pharm.*, cxix. 376, u. cxxv. 257.

WINCKLER.—*Repert. Pharm.*, lxi. 169, u. lxvij. 257.

PEPPER.

§ 298. Black pepper is the dried *immature* fruit of *Piper nigrum*, one of the *Piperaceæ*, or pepperworts.

White pepper is the same berry decorticated, or deprived of its outer and black husk or covering.

The pepperworts are a well-defined natural order, confined to the hottest parts of the world, and delighting in low places, valleys, and the banks of rivers. Although neither the number of its genera nor of its species is great, yet the whole order is remarkable for a variety of active and useful plants—*e.g.*, the aromatic black and long peppers, the astringent matico, the intoxicating *Macropiper methysticum*, the different varieties of cubebs, useful in the treatment of inflamed mucous membranes, and several other plants possessing medicinal properties,* belong to the natural order of *Piperaceæ*.

Black pepper itself is a climbing plant, attaining the height of from 8 to 12 feet; the berries—or, botanically speaking, "drupes" —are at first green, then red, and if left still longer ungathered, turn to black; but before this latter change takes place the berries are gathered by hand and dried in the sun, the result being an entire change of appearance; instead of a red, smooth berry, a black or reddish-black peppercorn, with the cortex contracted and shrivelled in such a manner as to form a veined network, is obtained. The plant is cultivated in various portions of the equatorial regions of the earth, the zone of cultivation being confined to the isotherms of 82°F. It would not, however, be strictly correct to say that this high mean annual temperature is essential, or even necessary; for the fact is, that it is produced principally in the cooler valleys, where the mean annual temperature does not, perhaps, exceed 70°Fahr.

The black pepper imported into this country principally comes from the islands of Malacca, Java, Borneo, and Sumatra. The commercial varieties are at least five—viz., Malabar, Penang, Sumatra, Trang, and Tellicherry, names indicating the localities whence they are derived. The differences which these different varieties of pepper present *to the eye* are evident enough when the several samples are at hand for comparison; but it takes a very practised observer to identify a solitary sample; and

* The *Artanthe eucalyptifolia* is used in Brazil in case of colic; *Piper parthenium*, used in menstrual disturbances; *Chavica betle* and *Siriboa* cause salivation, and decrease the function of the skin. Besides these, *Acrocarpidium hispidulum*, *Coccobryon capense*, *Artanthe adunca*, *Chavica adunca* and others, possess active and useful properties.

if samples of each of the kinds named were mixed together, it is doubtful whether an adept even could separate the berries again, identifying each sort with any correctness. The merchant, indeed, relies more upon the weight than the appearance; he takes a handful of peppercorns, and by long practice can tell in a moment whether it is a light or a heavy sample. Chevallier has determined the weight of what is technically called heavy, half-heavy, and light pepper. A litre of the first weighed 530 grms.; of the second, 512 grms.; of the third, 470 grms. That there is considerable difference in weight in the different berries is certain, for the writer carefully weighed 100 berries of each kind, with the following result:—

	Grammes.
100 peppercorns of Penang weighed . .	6·2496
100 ,, Malabar ,, . .	6·0536
100 ,, Sumatra ,, . .	5·1476
100 ,, Trang ,, . .	4·5736
100 ,, Tellicherry ,, . .	4·5076

If, then, quality is to be judged of by weight, Penang and Malabar may be bracketed together as standing first, Sumatra holding the second place, and Trang and Tellicherry bracketed together in the third. The general opinion of the trade is, that Malabar is really the heaviest, and possibly the samples of Penang which the writer possesses are unusually fine. The whole of the ground peppers of commerce are mixtures of different kinds of pepper; there is no such thing to be found in the shops as a pure ground Malabar or a pure ground Penang. The principal varieties mixed for household purposes and retailed are Malabar, Penang, and Sumatra; the first of these is the dearest.

The usual mixture, according to Chevallier, is—

33 per cent. of Malabar to give weight,
33 ,, Penang ,, strength, and
33 ,, Sumatra ,, colour.

The pepper thus mixed is either ground by the aid of large millstones, or in an apparatus perfectly analogous to a coffee-mill. The latter mode is far preferable to the former, as the friction of the stones develops considerable heat, and dissipates some of the aromatic principles. Pepper thus damaged by the heat of the mechanical operations is technically known as "burnt."*

Structure of Pepper.—A thin section of the pepper berry shows, from without inwards, (1.) a layer of elongated cells, large and distinct, having a central cavity, from which numerous lines

* From Art. Pepper in the Author's "Dict. of Hygiène."

radiate towards the circumference; (2.) a layer of small, angular, dark-coloured cells; (3.) a thin stratum of woody fibre and spiral vessels; (4.) a layer of large round cells; (5.) a tissue divisible into two layers, the outer consisting of coloured cells, the inner colourless, and really constituting a membrane.

Pepper contains an alkaloid (*Piperin*), a volatile oil, and an acrid resin, besides gum, starch, vegetable albumen, salts, and other substances.

Oil of Pepper has a specific gravity of from 0·86 to 0·99, and a boiling point 167° to 170°. It is a clear fluid, possessing a mild taste, and corresponds to the formula $C_{10}H_{16}$. Both white and black pepper contain a little more than 1 per cent. of this oil.*

§ 299. *Piperin*—($C_{17}H_{19}NO_3$)—was discovered by Oerstedt in 1819; it is found in white, long, and black pepper, in *Chavica officinarum*, in cubebs, in the berries of *Schinus. mollis*, and in the bark of *Liriodendron tulipifera*. When pure, piperin crystallises in colourless, brilliant, four-sided prisms; it is almost tasteless, and presents no alkaline reaction. It melts to an oily mass at about 100°, solidifying in a resinous form; is soluble in petroleum ether, alcohol, ether, the volatile oils, benzole, chloroform, and creosote. Concentrated nitric acid changes it into an orange-red resin; if this be treated with a solution of caustic potash, a blood-red colour is produced, and on boiling piperidin developed. Long heating with alcoholic potash decomposes piperin into piperidin and piperinate of potash, and the same substance is quickly developed by heating with soda lime.

Piperidin—$C_5H_{11}N$ (best obtained by dry distillation of piperin with three times its weight of soda lime)—is a clear, colourless, bitter, strongly alkaline fluid, which boils at 106°, and has an odour both of pepper and ammonia. It dissolves in water and alcohol in all proportions, and forms good crystalline salts with acids.

Piperic Acid—$C_{12}H_{10}O_4$—is obtained by boiling piperin with alcoholic potash, decomposing the piperate of potash by the addition of HCl, and subsequent purification of the acid by crystallisation from alcohol. The acid is in the form of yellow hair-like needles, some of which may be sublimed undecomposed; they dissolve easily in boiling alcohol, but are scarcely soluble in water.

Bucheim has given the name of "Chavicin" to a substance which he separated as follows:—Black pepper, after being exhausted of all matters soluble either in alcohol or water, was

* Dumas.—*Journ. Chem. Med.*, xi. 308.

treated with ether. The ethereal extract was shaken up with potash; on then separating and distilling the ether, *chavicin* is left behind, of the consistence of thick turpentine, and possessing a biting taste; it has not yet been obtained pure.

§ 300. *The Ash of Pepper.*—The following is an analysis of the ash of Tellicherry pepper:—

	100 grms. of Ash.
Potash,	24·380
Soda,	3·226
Magnesia,	13·000
Lime,	11·600
Iron,	0·300
Phosphoric acid,	8·470
Sulphuric acid,	9·613
Chlorine,	7·570
Carbonic acid,	14·000
Sand,	6·530

Of all of these constituents the sand is the most variable. The highest determination of sand which the writer has as yet met with, occurred in a sample of Penang pepper, which gave 9 parts of sand in every 100 of ash; but if we allow that a pepper ash may contain 10 parts in every 100 of sand, how on any theory, except that of wilful adulteration, can we account for the fact of the ground pepper of commerce yielding to the analyst an ash one-third or one-half of which is very commonly found to consist of sand? The iron, part of which is magnetic, the alkaline earths, the chlorine, the alkalies, all vary somewhat; but there is one constituent which is extremely constant, and may be of technical utility, and that is, the phosphoric acid. The phosphoric acid averages 8·5 per cent. of the ash. Pepper also has very minute quantities of carbonate; a sample of finely powdered Malabar pepper, treated with acid, and placed in an absorption apparatus connected with an aspirator, which drew through the solution perfectly dried carbonic-acid-free air, yielded ·657 milligramme of CO_2, or about ·143 per cent. of the ash; hence the 10 or 11 per cent. of CO_2 in the ash must be produced from the organic salts, &c.

Nitrates and Nitrites in Pepper.—Comparatively few observations of the amount of nitrates and nitrites in organic substances are on record: it is a subject of some scientific interest, especially since it has been observed that nitrates and nitrites are decomposed in the presence of free oxalic acid. Whether the determination of nitric acid will be of service to the food-analyst or not is unknown; it certainly may be so, if it be found that a substance rich in nitrates is fraudulently mixed with one poor in nitrates.

			Calculated as Nitric Acid. Grms.
100 grms. undried Penang pepper yield			0·04470
,,	,,	Malabar ,,	0·03858
,,	,,	Tellicherry ,,	0·08860
,,	,,	Sumatra ,,	0·06560
,,	,,	Trang ,,	0·11870

§ 301. *General Composition of Pepper.*—In a sample of Penang pepper analysed by the writer :—

	Per cent.
Volatile oil,	1·04
Acrid resin,	1·77
Piperin,	5·17
Substances soluble in water, gum, starch, and other matters, subtracting ash,	14·74
Substances insoluble in alcohol and water,	67·75
Water,	9·53
	100·00

The following table exhibits some analyses made by the writer in 1876 of genuine black peppers, and may be compared with similar determinations of white and long peppers :—

TABLE LII.—GENERAL COMPOSITION OF COMMERCIAL PEPPERS.

	Hygroscopic Moisture	Piperin in Pepper dried at 100°.	Resin in Pepper dried at 100°.	Aqueous Extract in Pepper dried at 100°.	Ash in Pepper dried at 100°.	
					Soluble in water.	Total.
	Per cent.	Per cent.	Per cent.	Per cent.		
Penang,	9·53	5·57	2·08	18·33	2·21	4·18
Tellicherry,	12·90	4·675	1·70	16·5	3·38	5·77
Sumatra,	10·10	4·702	1·74	17·59	2·62	4·31
Malabar,	10·54	4·632	1·74	20·37	3·45	5·19
Trang,	11·66	4·600	1·70	18·17	2·53	4·77
White Pepper, Commercial,	10·30	5·600	2·05	...	0·56	1·12
Long Pepper,	...	1·800	0·80	16·82	4·47	8·30

§ 302. *Analysis of Pepper.*—The ash and hygroscopic moisture are estimated in the usual manner. The commercial value of a

pepper ought to bear a definite relation to the piperin and acrid resin, so that the latter constituents are the most important to determine.

There are two methods of estimating the piperin and resin:—The one is to exhaust thoroughly the finely powdered pepper with strong alcohol, evaporate, and weigh the extract, which practically consists of nothing but resin and piperin. The latter is now separated by digestion with soda-lye, which dissolves the resin, leaving insoluble the piperin, which may be redissolved in strong alcohol, filtered, evaporated, and weighed as piperin. The other process, which, on the whole, is preferable, is to dissolve the piperin out by petroleum ether, and purify the extract thus obtained as before. Some chemists, again, first extract with alcohol, and then treat the alcoholic extract with petroleum ether, a method which is equally valid, but not, perhaps, so convenient as the second given.

§ 303. *Adulterations of Pepper.*—Pepper has been adulterated for at least two centuries and a half; for Pierre Pomet,* writing in 1614, says: "As the greatest part of pepper, white as well as black, is sold '*battu*' (that is to say, powdered), it should only be bought of honest merchants; because all the pepper the retailers sell is no other thing for the white than '*épices d'Auvergne blanchées*,' or rather black pepper whitened with ground rice; the black is only the dust either of the crust of bread, grey Auvergne spices, or manignette."

The list of the adulterations enumerated by authors is an extraordinary one. Linseed meal, rice, pepper leaves, mustard, wheat flour, sago, woody fibre, chillies, rape-seed, potato, spices, capsicum, manignette (otherwise known as Guinea pepper), chicory, rye, powdered leaves of the laurel, which had been previously used to wrap round extract of liquorice, the stones from olives, bone-dust, marine salt, and various mineral adulterations, are all said to have been detected.

However various may be the adulterations in France (where, Chevallier tells us, in Paris alone he is acquainted with a manufactory producing 1200 to 1500 kilogrammes annually of a mixture sold solely for the purpose of adulterating pepper), the only common adulterations of this country are what are known in the trade as P.D., H.P.D., and W.P.D., abbreviations for pepper-dust, hot pepper-dust, and white pepper-dust. The first, or P.D., used to be principally composed of faded leaves, but linseed-meal is now preferred; H.P.D. is chiefly the husks of mustard and W.P.D. is ground rice. To all these we must add sand,

* Pomet: "Hist. Gén. des Drogues," 1735.

which is most certainly used, though whether derived from the sweepings of the shops, or added as sand, is by no means clear. The sand, of course, influences the weight of the ash, which should never exceed 7 per cent.

Dr. Hassall made some determinations of the ash of some fifteen or sixteen commercial samples of black pepper; of these only one was under 5 per cent., the percentages of the other fifteen being distributed as follows:—

One	gave between	5 and 6	per cent.	of ash.
Three	,,	6 and 7	,,	,,
Three	,,	7 and 8	,,	,,
Seven	,,	9 and 10	,,	,,
One	,,	11 and 12	,,	,,

It is difficult to believe that more than 2 per cent. of unavoidable mineral dust can get into the pepper by grinding, &c., and the inference naturally is that most of the above samples were adulterated. The maximum percentage of ash from genuine pepper which the writer has obtained is 5·3 per cent.

Besides the formidable list of adulterations already mentioned, the berry itself is not free from manipulation; for, as the merchant judges by the weight of the sample, means are taken to render the lighter sorts equal in weight to the heavy Malabar and Penang, and in order to do this they are macerated in tubs of brine for twenty-four hours, and thus impregnated with salt and water find their way into the market as Malabar; but such samples are quickly recognised by the astute merchant; and the high chlorides, the high ash, the great amount of humidity, could hardly fail to reveal their nature to the analyst.

As coffee has been cleverly imitated by chicory pressed into the shape of the coffee-berry, so by pressing various pastes into the shape of the pepper-berry has pepper been imitated. Of this adulteration there is the most undoubted evidence. Accum noticed artificial peppercorns made of oilcake, common clay, and Cayenne pepper, and Chevallier, in a recent paper, states that in 1843 he was requested to examine a sample taken from forty bales, in which he found from 15 to 20 per cent. of artificial pepper, composed of pepper-dust, bran, and other matters.*

LEGAL CASE.

Pepper adulterated with Sand, and containing Sago.

At the Cardiff Police-Court, 1875, a grocer was summoned for selling adulterated pepper. The town-clerk conducting the prosecution, had sent a sample to Dr. Hassall, who stated the quantity of ash found in genuine pepper

* Art. Pepper in author's "Dict. of Hygiène."

as varying from 3·843 per cent. to 4·061 per cent., the highest amount found being 5·25 per cent. No genuine ground pepper as sold should contain 5·5 per cent. of ash. The sample of pepper sent up to him in this case for analysis contained 3 per cent. of sago, and 12 per cent. of earthy matter, one-half of which was silica. The presence of sago he attributed to accident, the quantity being so small; and the presence of earthy matter and sand to the improper manner of drying the pepper berries, and not to adulteration.

Mr. J. W. Thomas, the local analyst, gave, as the result of his analysis, that the pepper contained sago, rice, and arrowroot, with a large quantity of woody fibre and dust, other than that of pepper, the quantity of this ash being 10·5 per cent.

A third analyst gave as the result of his analysis that the pepper contained 3 per cent. of starchy matter, and 10 per cent. of ash, one-half of which was sand. He considered the pepper genuine, but of an inferior quality. The presence of starchy matter was due, he believed, to accident or carelessness in those who had the handling of the pepper before being sold. The quantity was so small that it was scarcely probable it had been added for the purpose of adulteration. In reply to questions from the Bench he stated that he considered the sample of pepper a very bad one, but it was genuine pepper. The presence of even 25 or 30 per cent. of ash, such as was found in this case, would be no proof of adulteration. The earthy matter found there would most probably be the result of the dust and other matter adhering to the berries when exposed to the atmosphere to dry.

On cross-examination, this gentleman considered that the ash was in excess of what might be expected to be found, and would only be discovered in inferior samples. He then explained that the pepper berries, after being dried, would naturally have particles of earthy matter adhering to the husks. After being dried they were packed in bags, and in the course of time the husk would probably separate from the corn, and the dust becoming dry would, by force of gravity, fall to the bottom. The sample of pepper at the top of the bag might not contain more than 4 per cent of earthy matter, but that at the bottom 20, and although the 20 per cent. were found in the sample taken from the bottom, that would be no proof of adulteration.

The Bench dismissed the case.

The author is of opinion that the Bench, in the face of the evidence, could scarcely do otherwise than dismiss the case; but the magistrates were certainly grievously misled by the witnesses. How any one with the least knowledge of the subject could declare a sample of pepper containing 20 per cent. of earthy matter to be genuine pepper, and of the nature and quality demanded by the purchaser, is incredible. Without doubt, the pepper in this case came within the meaning of the Act, and was adulterated. If such a defence as that of sand falling from the top to the bottom of a bag be once admitted, it would come to this, that the last few ounces may be found to contain half their weight of sand, and yet be legally sold as pepper —which is obviously absurd.

BIBLIOGRAPHY.

The general treatises on adulteration, see page 43, have nearly all articles on "pepper."

Anderson.—*Ann. Chem. Pharm.*, lxxv. 82; lxxxiv. 345.
Babo and Keller.—*Journ. Prac. Chem.*, lxxii. 53.

BLYTH, A. WYNTER.—*Chem. News*, xxx. 170; *Ann. d'Hygiène*, 1875, t. xliv.; *Proc. Soc. of Analysts*, Vol. I., 1876.
BOUCHARDAT.—*Union Pharm.*, 1873, t. xii., p. 497.
CAHOURS.—*Ann. Chim. Phys.* [3], xxxviij. 76.
CHOULETTE.—*Journ. Chim. Méd.*, 4e série, 1857, t. vij., p. 441.
CHEVALLIER.—*Ann. d'Hygiène*, 1875.
COOLEY.—"Dict. of Pract. Receipts." London, 1872.
FLUCKIGER and HANBURY.—"Pharmacologia." London, 1875.
GERHARDT.—*Compt. Chim.*, 1849, 357.
HINTERBERGER.—*Ann. Chem. Pharm.*, lxxvij. 204.
HUSEMANN.—"Die Pflanzenstoffe." Berlin, 1871.
MERAT et DELENS.—"Dictionnaire Universel de Matière Médicale et de Thérapeutique." Paris, 1829-1846.
PELLETIER.—*Ann. Chim. Phys.*, [2], xvj. 344; li. 199.
POMET.—"Histoire des Drogues." Paris, 1735.
PUEL.—*Journ. Chim. Méd.*, 4e série, 1875, t. iij., p. 739.
SAVARY DES BRUSLOUS.—"Dictionnaire du Commerce."
STENHOUSE.—*Ann. Chem. Pharm.*, xcv. 106.
STRECKER.—*Ann. Chem. Pharm.*, cv. 317.
VARRENTRAP and WILL.—*Ann. Chem. Pharm.*, xxxix. 283.

CAYENNE PEPPER.

§ 304. Cayenne pepper consists of the powdered pods or seed vessels of the *Capsicum annuum*, a plant belonging to the natural order *Solanaceæ.* It is a native of America, but is also cultivated, to a slight extent, in the greenhouses of England and other European countries. It is sold entire under the name of *Chillies.* The microscopical structure of the capsules is somewhat peculiar: the epidermis is formed of cells the walls of which are thick, flattened, tortuous, well defined, and punctuated here and there; frequent drops of a reddish-orange oil occur, especially in the parenchyma, which is formed of thin-walled, rounded cells. The envelope of the grain itself, when cut in thin vertical sections, presents a very singular appearance, that of radiating dentiform processes, the apex of each being apparently fixed in the outer membrane. The substance of the seed proper is composed of small angular cells, with thick colourless walls, filled with granules and a yellow-orange oil, but without starch.

Cayenne pepper, as met with in commerce, is in the form of a somewhat coarse, brick-dust like powder, the least particle of which, if heated strongly, volatilises a very acrid vapour, causing intense irritation of the throat. This sensation can be produced by so minute a portion of cayenne, that any foreign substance mixed with it could in this way be detected; it would be only necessary to separate carefully, by the aid of the microscope and

a camel's-hair brush, all particles of cayenne, and heat the portion suspected; if no acrid vapours were given off, the substance could not be cayenne. This intense acridity appears to be due to a body recently discovered by Mr Thresh, and named by him Capsaicin.

§ 305. *Capsaicin*—($C_9H_{14}O_5$), specific gravity 1060—is in the form of minute crystals, which melt at 55°·5 (138°F.), volatilise unchanged at 115°·6 (240°F.), and at 120° (248°F.) become brownish-black. It may be obtained by exhausting cayenne by petroleum, evaporating the petroleum, and treating the extract thus obtained by dilute solution of potash; on now saturating the solution with carbonic anhydride, it is precipitated in very small crystals. It dissolves slightly in cold, and more readily in boiling, water; is easily soluble in alcohol, proof spirit, ether, amylic alcohol, acetic ether, acetic acid, benzine, the fixed oils, and solutions of the alkalies. It dissolves slowly in turpentine and carbonic disulphide; when pure, petroleum does not dissolve it readily, but the presence of the red oil in the pepper increases its solvent powers; it is totally insoluble in solutions of the carbonates of the fixed alkalies, and in ammonia. Silver nitrate gives a precipitate with alcoholic solutions of capsaicin; it also yields white precipitates with barium and calcium chlorides. It is powerfully pungent, causing, if volatilised, severe fits of coughing.

It would appear that capsaicin is not contained in the substance of the seed; for if the pericarp be carefully separated, the seeds are entirely devoid of acrid taste.

Mr. Thresh has also described a conium-like alkaloid, obtained by exhausting the pericarp with benzine, evaporating, dissolving in ether, shaking the solution with dilute sulphuric acid, partially neutralising with barium carbonate, and evaporating to a small bulk. Some red fat now separates, and after the removal of this (upon adding an excess of alkali, shaking with ether, and evaporating) a brown residue is obtained, smelling like conium, and giving precipitates with Nessler reagent, iodine, and iodides of potassium and cadmium.

The acrid oil *Capsicol*, *Capsicin*, and other substances described by Bucholz, Bracannot, Buchheim, &c., are undoubtedly mixtures. The general composition of cayenne pepper may, however, be gathered from the following analyses, one made in 1816 by Bucholz, the second in 1817 by Bracannot, of course neither taking cognisance of capsaicin:—

BUCHOLZ'S ANALYSIS.

Acrid soft resin (capsicum),	4·0
Wax,	7·6
Bitter aromatic extractive,	8·6
Extractive, with some gum,	21·0
Gum,	9·2
Albuminous matter,	3·2
Woody fibre,	28·0
Water,	12·0
Loss,	6·4
Fruit of *Capsicum annuum*, without seeds,	100·0

BRACANNOT'S ANALYSIS.

Acrid oil,	1·9
Wax and red colouring-matter,	0·9
Brownish starchy matter,	9·0
Peculiar gum,	6·0
Animalised matter,	5·0
Woody fibre,	67·8
Salts: extract of potash, 6·0; phosphate of potash and chloride of potassium, 3·4,	9·4
Fruit of *Capsicum annuum*,	100·0

The hygroscopic moisture ranges in different samples from 10 to 13 per cent. The writer analysed several samples of genuine cayenne, and the mean of these analyses was as follows:—

	Per cent.
Aqueous extract of dried cayenne,	32·1
Alcoholic extract,	25·79
Benzole extract,	20·00
Ethereal extract,	10·43
Ash,	5·693 (soluble, 3·32)
Total nitrogen in 100 grms.,	2·04

Hence the ash of cayenne should not exceed 6 per cent.; it should yield at least one-quarter of its weight to alcohol, and from 9 to 10 per cent. to ether.

§ 306. *The Adulterations of Cayenne* usually enumerated are: all kinds of red mineral powders, from brick-dust to cinnabar, and a few starches. There does not appear, however, to have been any conviction recently for the adulteration of cayenne, and the numerous samples the writer has examined were all genuine. Most of these additions would be easily detected in the ash, or by the microscope. Cinnabar is highly improbable; for its detection, see "Mercury," in the second volume of this work.

BIBLIOGRAPHY.

BLYTH, A. WYNTER.—Art. Capsicum, "Dict. of Hygiène."
BRACANNOT.—*Ann. Chim. Phys.*, [2], vj., t. 124.
HASSALL.—"Food and its Adulterations."
LANDESER.—*Viertelj. Pract. Pharm.*, iii. 34.
THRESH, J. C.—*Pharm. Journ.*, [3], 309, p. 941 ; [3], 315, 1876, p. 21 ; [3], 326, p. 259 ; [3], vij. 473.
WITTING.—*Repert. Pharm.*, xiii. 366.

THE SWEET AND BITTER ALMOND.

§ 307. The sweet almond, the seed of *Amygdala communis*, and the bitter almond, the seed of *Amygdalus communis*, var. *Amara*, enter either in whole or in part into so many articles of food (such as sweetmeats and pastry, and as a flavouring ingredient into certain drinks), that it is absolutely necessary to be acquainted with their chemical composition. Both varieties of almond agree in containing about 50 per cent. of a bland fixed oil (consisting chiefly of olein, and liable to become rancid), as well as an albuminous principle, emulsin, sugar, gum, and woody fibre; but only in the bitter almond is found, in addition to the foregoing, *amygdaline*.

§ 308. *The Oil of Almonds* is a thin fluid oil, of a clear yellow colour, specific gravity 0·914 to ·920, not coagulated by a cold of $-10°$; at $-16°$ it becomes cloudy, and at $-22°$ it solidifies to a white butter. Oil of almonds appears to be rather frequently adulterated with other oils.

2·5 drops of the oil, shaken with an equal bulk of nitric acid (specific gravity 1·20) and bisulphide of carbon, should not show any colour after standing a few minutes; if it becomes within half an hour yellow, or reddish-yellow, the change indicates oil from *cherry* or *apricot kernels*.

The following test will detect drying oils :—Dissolve one part of starch in 3 parts of warm nitric acid, of 1·20 specific gravity, and warm in a capacious vessel over the water-bath with 10 parts of almond oil, until all evolution of gas ceases. The oil after cooling is within two days changed into a warty, crystalline, greasy mass of elaidin. Should it, however, contain a drying oil (*poppy*, for example), it either remains quite fluid or semi-fluid, according to the proportion of the adulterant present. The colour of the elaidin is also a guide; that produced by the sweet almond is pure white, by the bitter, yellowish-white, and by the small or inferior kinds of almonds, brownish-yellow; if the elaidin

should be red, it denotes adulteration of some foreign oil, especially of *sesame*.

Pure almond oil dissolves in 25 parts of cold and 6 of hot alcohol. The above tests, and in addition the low temperature required for congelation, should detect all ordinary adulterations.

§ 309. *Amygdaline* ($C_{20}H_{27}NO_{11}$) is a glucoside, discovered in 1830 by Robiquet and Boutron-Charlard. It may be extracted from almond-cake by boiling alcohol of 95 per cent., and then precipitated from the somewhat concentrated alcoholic solution by ether. Amygdaline* crystallises from 80 per cent. alcohol in colourless glittering scales, containing two atoms of water: it can also be obtained in crystals. Amorphous amygdaline of the before-mentioned cherry-laurel leaves and buckthorn bark is best obtained by the following method:—The dried buckthorn bark is boiled with absolute alcohol, agitated with lead oxide, and evaporated to dryness. Dried in a vacuum over SO_4H_2 it forms a brittle, yellow, transparent, resin-like mass, which, when heated to 100°, becomes dark-brown; it can be dissolved by boiling alcohol and by water, but is insoluble in ether. Although amorphous, it is a crystalloid with three atoms of water, as proved by dialysis from water or weak spirit, but in such a case it loses one atom if dried over sulphuric acid. At 100° to 120° it may be obtained anhydrous.

Amygdaline possesses no smell; it has a slightly bitter taste; its reaction is neutral, and it polarises to the left $[\alpha]_r = -35{\cdot}57°$. It dissolves in all proportions in boiling water, and in 12 parts of cold of 10°; requires 148 parts of alcohol, specific gravity 0·939, 904 parts of alcohol, specific gravity 0·819, if cold—but if boiling, 11 parts of the first and 12 of the last; it is insoluble in ether. It melts at 120°, and begins to carbonise at 160°, when it develops a caramel smell, and is at length fully destroyed.

* Lehmann, in his recent elaborate researches, found the method of Liebig and Wohler the best for obtaining *crystalline* amygdaline. The process consists in boiling the substance with strong alcohol (of 94 to 95 per cent.) twice successively, after having first removed the fixed oil by petroleum benzine, concentrating to about one-half or one-sixth of its volume; and then adding ether, which precipitates the amygdaline, and removes any of the remaining fixed oil. Lehmann obtained from

Bitter almonds, . .	2·5	per cent. crystallised amygdaline.
Cherry-kernels,	0·82	
Plum-kernels,	0·96	,,
Apple-seeds,	0·60	,,
Peach-kernels, .	2·35	,, ,, ,,
Cherry-laurel leaves, .	1·38	per cent. amorphous amygdaline.
Bark of *Rhamnus frangala*,	0·7	,, ,, ,,

Both of these latter substances contain hydrocyanic acid ready formed.

Amygdaline, by the action of dilute hydrochloric acid, splits up into glucose and mandelic acid, volatile oil of almonds, and formic acid. If boiled with solutions of potash or baryta it forms ammonia and amygdalic acid. The most interesting decomposition is, however, that which takes place by the action of emulsin; it then breaks up into volatile oil of almonds, hydrocyanic acid, and formic acid. (See *Prussic Acid*, in the second volume of this work.)

Volatile Oil, or Essence of Almonds, does not exist as such in the bitter almond; it is, as above explained, the result of the decomposition of the amygdaline. The oil of almonds, when properly purified from prussic acid, is identical with the hydride of benzole, C_7H_5OH. It is colourless, thin, turning a ray of polarised light to the right, of a peculiar, pleasant odour, and a burning aromatic taste. Its specific gravity is 1·043 to 1·07, usually 1·06 (*Hirsch*). Its boiling point is 180°. By the action of light and air it is gradually oxidised into benzoic acid. It is soluble in equal parts of alcohol, 0·830 specific gravity, and in about 30 parts of water. The ethereal or volatile oil is officinal in the French, Swiss, and Norwegian pharmacopœias. The ethereal oil is much adulterated. The analyst will specially look for alcohol, prussic acid, nitrobenzine, and ethereal oils.

If *alcohol-free*, the addition of an equal weight of fuming nitric acid produces no effervescence, and after two or three days the mass becomes emerald green, and crystals of benzoic acid appear. On the other hand, if it contain alcohol from 0·08 per cent. upwards, there is immediately a strong effervescence. Some of the tests given for alcohol at pp. 375-376 may also be of service.

The detection and estimation of *prussic acid* in the essence is carried out on the principles detailed in the article on *Prussic Acid* (see vol. ii.)

Nitrobenzine is indicated when the essence is not entirely soluble in a solution of bisulphate of potash, and the specific gravity is higher than 1·07, the specific gravity of nitrobenzine being 1·20 to 1·29; the boiling point will also be raised. In such a case nitrobenzine should be specially tested for, by changing it into aniline by reducing agents. For this purpose 10 parts of dilute sulphuric acid (specific gravity 1·117) may be added to 10 of granulated zinc and 1 part of the essence. At the end of two hours (after frequent agitation) the fluid is passed through a moistened filter, and a crystal of chlorate of potash added to the filtrate with a drop of concentrated sulphuric acid. If a violet or red colour is produced, it is due to the presence of an aniline salt, produced from nitrobenzine; but if there is no coloration, nitrobenzine must have been absent.

Another special method used for the detection of nitrobenzine was proposed by Maisch:—1 grm. of the essence is dissolved in twelve times its volume of alcohol, ·75 of caustic melted potash is added, and the whole heated until the liquid is diminished to about one-third. The pure essence, on cooling, is of a light brown colour, and dissolves entirely in water; but if nitrobenzine is present, the residue is brown, crystalline, and insoluble in water.

The action of sodium on the essence may also be utilised as a test:—Pure almond essence, when treated with sodium, gives white flocks; if nitrobenzine should be present, the sodium is immediately covered with yellow or brown flakes, according to the amount of adulteration; if the percentage rises as high as 0·30 to 0·50, the whole liquid after a minute becomes thick and opaque. (*Dragendorff.*)

However, the action of potash alone on a sample adulterated with nitrobenzine is tolerably conclusive. If one grm. of the essence is treated in a test-tube with half its weight of pure caustic potash, a yellow coloration is produced, should the essence be pure; but if nitrobenzine be present, the tint soon becomes yellowish-red, and at the end of a minute green. On the addition of a little water, the mixture separates into two layers, of which the lower is yellow and the upper green, the latter changing in the course of a day into red. Most foreign *ethereal oils* may be detected by the bisulphate of soda test:—If a little of the pure essence be dropped into a warm solution of this salt, of from 1·24 to 1·26 specific gravity, shaken, and then diluted with hot water, it is fully dissolved; other essences, on the contrary, are insoluble.

BIBLIOGRAPHY.

Bette.—*Ann. Chem. Pharm.*, xxi. 211.

Bourgoin.—Falsification de l'essence d'amandes amères par le nitrobenzole? *Journ. Pharm. et Chim.*, 4e série, 1872, t. xv., p. 281.

Fluckiger.—*N. Jahrb. Pharm.*, xxxiv. 202; Testing of Bitter Almond Oil, *Pharm. Journ.*, Oct., 1870, p. 321.

Hirsch—"Die Prüfung der Arzneimittel." Berlin, 1875.

Husemann.—"Die Pflanzenstoffe." Berlin, 1871.

Lehmann.—*Proc. Amer. Pharm. Assoc.*, 1875, 437.

Maisch.—Falsification de l'essence d'amandes amères. *Journ. Pharm. et Chim.*, 3e série, 1858, t. xxxiv., p. 75.

Redwood.—Means of recognising the Purity of Essence of Almonds. *Pharm. Journ.*, and *Journ. Pharm. et Chim.*, 1858.

Robiquet and Boutron Charlard.—*Ann. Chem. Phys.* [2], xliv. 352 *Journ. Pharm.*, [2], xxiii.; *Ann. Chem. Pharm.*, xxxi. 211.

SOUBEIRAN.—"Dictionnaire des Falsifications." Paris, 1874.
VAN DEN CORPIT.—Sur la falsification de l'essence d'amandes amères. *Journ. Chim. Méd.*, 4e série, 1855, t. i., p. 585.
WICKE.—*Ann. Chem. Pharm.* lxxix. 79; lxxxi. 241; lxxxiii. 175.
WINCKLER.—*Rep. Pharm.*, lxv. 1.
WOHLER and LIEBIG.—*Ann. Chem. Pharm.*, xxii. 1.

ANNATTO.

§ 310. Annatto is a colouring-matter obtained from the seeds of the *Bixa orellana*, chiefly prepared in Brazil and Cayenne. Although not used itself as a food, it enters into several articles of consumption, and has been employed to colour milk, butter, and cheese.

Microscopical Characters.—When annatto is examined by the microscope, the outer red portion presents an almost homogeneous appearance, and the surface of the seed proper consists of narrow or elongated cells or fibres vertically disposed, while the inner white portion consists of cells filled with starch corpuscles, well defined, of medium size, and resembling in the elongated and stellate hilum the starch granules of the pea and bean.

In manufactured unadulterated annatto, but little structure is met with. Portions of the outer cells may be seen; and in those specimens, which in the course of their preparation have not been subjected to the action of boiling water, a few starch granules may be noticed.

Since this is the case with annatto itself, we can the more easily detect the presence of most foreign vegetable substances, such as turmeric powder, the starch of wheat, rye, barley and sago flours. The salt and alkali present in the annatto generally greatly alter the appearance of the turmeric. Most of the colouring-matter of the cells is discharged, so that the starch corpuscles contained within them become visible. Loose starch granules of turmeric may also be frequently seen, and in consequence of the action of the alkali much enlarged.

§ 311. *Chemical Composition of Annatto.*—Dr. John found the pulp surrounding the fresh seed to consist of 28 parts of colouring resinous matter, 26·5 of vegetable gluten, 20 of ligneous fibre, 20 of colouring extractive matter, 4 formed of matters analogous to vegetable extractive, and a trace of spicy and acid matters. The colouring-matter consists of a red substance—*bixin*, associated with a yellow, *orellin;* the latter has been as yet but little studied.

Bixin, $C_{15}H_{18}O_4$, when pure, is an amorphous, resinous, cinnabar-red substance. It is scarcely soluble in water and bisulphide of carbon, soluble in about 89 parts of cold, and in 25 of hot, alcohol; in 345 parts of ether, in 93 of chloroform, and also in the caustic and carbonated alkalies. The alcoholic solution is coloured orange-red by lead acetate, brownish-yellow by chloride of mercury and acetate of copper, brown-red by chloride of iron, and it is precipitated yellow by stannous or stannic chloride; concentrated sulphuric acid produces a deep blue. A solution of bixin in an alkaline liquid, on neutralisation with an acid, gives a precipitate of the resin, and in this way it may be purified.

§ 312. *Adulterations.*—Annatto is one of the most adulterated substances met with in commerce, the adulterants being both organic and inorganic. The organic substances used are—turmeric, rye, barley, and wheat flours. The inorganic—sulphate of lime, carbonate of lime, salt, alkali, an oily substance (probably soap), red ferruginous earths (mostly venetian red), red lead, and copper.

When large quantities of flour and lime are used, the colour of the annatto is so reduced that it becomes necessary to use salt, alkalies, and the red earths, to restore it to its original standard. Salt heightens the intensity of vegetable reds, hence its use. Lead is probably introduced into the annatto through the venetian red used. Copper is added to prevent the annatto becoming attacked by fungi.

The following is an analysis by the writer of a fair commercial sample.

No. 1. The sample was in the form of a paste, colour deep red, odour peculiar, but not disagreeable:—

Water,	24·2
Resin	28·8
Ash,	22·5
Starch and Extractive Matter,	24·5
	100·0

The following is an analysis of an adulterated sample. It was in the form of a hard brown cake, texture hard and leathery, odour disagreeable:—

Water,	13·4
Resin,	11·0
Ash—consisting of Iron, Silica, Chalk, Alumina, and Salt,	48·3
Extractive Matter,	27·3
	100·0

§ 313. The *Analysis of Annatto*, as may be gathered from the preceding description, principally resolves itself into a determination of the ash and an estimation of the resin. The former is determined in the usual way, the latter by exhausting the sample by boiling alcohol, getting rid of the spirit by evaporation, and then redissolving the extract thus obtained in an alkaline solution, and finally precipitating the nearly pure resin by careful neutralisation with an acid.

BIBLIOGRAPHY

BLYTH, A. WYNTER.—"Dict. of Hygiène." London, 1876.
BOLLEY and MYLIUS.—*Chem. Centralbl.*, 1865, 40.
COOLEY'S "Dictionary of Practical Receipts." London, 1872.
JOHN.—*Chem. Schrift.*, ii. 73.
STEIN, W.—*Journ. Pract. Chem.*, also *Chem. Centralbl.*, 1867, 812

OLIVE OIL.

§ 314. Olive oil, as indicated by its name, is extracted from olives, that is, the fruit of the *Olea Europea.* Olives furnish from 20 to 25 per cent. of their weight of oil.

Pure olive oil is pale yellow, or yellowish-green, perfectly transparent, with a faint agreeable odour and taste; it commences to thicken and solidify at from $+6°$ to $+8°$, and being one of the oils least liable to become rancid, is used for a variety of technical purposes as well as for food. The consumption of this oil in France as a food or as an adjunct to food, is especially large in proportion to the population; in Paris alone more than 5000 hectolitres being consumed yearly. According to König, the elementary composition of olive oil is, carbon 76·67 per cent., hydrogen 11·95 per cent., and oxygen 11·38. By saponifying with lead oxide, König obtained 2·01 per cent. of glycerine, and 50·92 per cent. of oleic acids; he returns the rest as palmitic and stearic acids. Van der Becke found, when he saponified with lead oxide, 3·76 per cent. of glycerine, but saponified with alcoholic potash 6·41 per cent. of glycerine.

§ 315. *Adulterations of Olive Oil.*—The adulterations of olive oil have excited more public attention on the Continent than in this country;* but there is little doubt that the oil is very

* See a letter from the French Minister of Agriculture to the Academy. *Comptes Rendus*, lxxxix., p. 518.

extensively tampered with, oils from cheaper subjects being substituted or added in large proportion. The number of processes which have been proposed for the detection of adulteration of oils in general, and olive oil in particular, is embarrassing to the student, and the results in general are disappointing, all, without exception, only detecting with certainty comparatively large admixtures, and being deficient in that precision which an English court of justice requires. However, the interesting observation made by Van der Becke, that when various fats are saponified by lead oxide, lime, and potash, very different amounts of glycerine are obtained, has led to the invention of quantitative processes, enabling the analyst to detect with certainty foreign admixtures.* Thus Van der Becke saponified the following fats, and obtained percentages of glycerine as under—

	Lead Oxide.	Lime.	Potash
Cocoa butter, . .	·23	2·19	5·99
Tallow, . . .	·13	2·43	7·84
Butter, . . .	7·93	7·99	10·59
Lard, . . .	6·60	8·27	9·27
Olive oil, . . .	3·76	...	6·41
Rape-seed oil, . .	4·20	...	4·58
Linseed oil, . .	4·40	...	6·20

It is to be hoped that further work will be done in this direction.

The processes now used for the detection of adulteration in olive oil may be divided into physical and chemical.

(1.) *Physical.*—The spectrum of olive oil shows an absorption of the blue and violet rays, a fine line in the green, and a distinct deep band in the red. B. Nickels† has proposed to use these facts in order to detect the admixture of cotton-seed oil, which gives no bands, and on comparing a definite measured stratum of the suspected oil with the same thickness of genuine oil, by the difference in the intensity of the absorption adulteration will be indicated.

Rousseau's Diagomètre.—According to Rousseau, olive oil conducts electricity 675 times better than any other vegetable oil, and he has arranged a most ingenious galvanic apparatus for the purpose of detecting the adulteration of the oil by this means. The apparatus essentially consists of a galvanometer connected with a dry pile, the needle works on a delicate pivot fixed in a resin plate, and there is a circle divided into degrees marking the amount of deviation. The oil to be tested is placed in a

* *Zeitschrift für Analytische Chemie*, 1880, p. 291.
† *Pharm. Journ.*, 1881, May.

small cup, and the current transmitted; the better the oil conducts electricity, the greater the deviation of the needle from the zero point at which it is applied to a metallic upright connected with the oil by a wire.

Cohesion Figures.—This physical process is described at p. 292. A genuine sample of the oil must be at hand, and drops of this and of the oil to be tested must be allowed to fall from the same height, and, in a word, under exactly similar conditions, on to the still surface of water side by side, when a good judgment may be formed from the pattern of the film, and its similarity or dissimilarity to that of pure oil.

Specific Gravity.—The specific gravity is best taken in the ordinary way by a specific gravity bottle at 15°. The following table shows the density of olive oil and that of a few of the oils, such as poppy and cotton-seed, which are often used for the purpose of adulteration.

	Specific gravity, taken at 15·0°
Olive oil,	·9176
Poppy oil,	·9243
Cotton-seed oil,	·9310
Sweet almond oil,	·9180
Arachis oil (from the *Arachis hypojea*),	·9170
Colza oil,	·9136
Sesame oil,	·9230
Nut oil (*Juglons regia*),	·9260
Beech-nut oil,	·9225

It is evident that the specific gravity will only be a conclusive proof when the adulterant has a gravity much higher or lower than that of olive oil. With mixtures of an oil like, for example, arachis oil, of similar density, a determination of the gravity will not of itself throw any light upon the purity of the sample. Nevertheless, a determination of specific gravity should be always made as a matter of course, since it may confirm other tests, and in every case a knowledge of the density is important.

(2.) *Chemical Tests—Oxidation.*—The so-called "elaidin" test, in which the oil is treated with nitric acid and copper turnings, and thus by oxidation transformed into a solid mass, is not of very much value as a test for purity, though possibly, by acting on a known pure sample, and examining it side by side with the suspected oil, valuable information may be obtained. The old-fashioned nitric acid test, according to Mr. Michael Couroy, applied as follows, is of some service—1 part of strong nitric acid is mixed with 9 parts of the oil, and warmed until the action is fairly set up; the flame is then removed, and the mixture stirred with a glass rod until the oxidation is over. Pure olive

oil thus treated sets into a pale straw-coloured, hard mass in an hour or two; while cotton and other seed oils assume a deep orange-red colour, and do not set like olive oil. He asserts that there is a regular gradation of colour, according to the percentage of adulteration, and that by imitation mixtures approximate quantitative results may be obtained. The amount of delicacy under the most favourable circumstances does not appear to be more than 5 per cent.

A similar oxidation test is that of saturating sulphuric acid with hyponitric acid, adding it to the oil, and noting the time in which it sets to a solid mass; 7 grms. of the acid thus prepared are added to 9 grms. of oil; at 5° olive oil sets to a solid mass in ten minutes, and after twenty-four hours is a white hard mass.

Arachis oil, rape oil, and cotton oil get solid later in about an hour; while sesame oil after twenty-four hours is still as soft as honey. Mixtures of oils of slow solidifying properties with olive oil, are in proportion to their percentages slower of coagulation. Here, as in all other cases, a pure sample of oil for comparison is an essential. M. Lipowitz has proposed the following as a special test for poppy oil: If 1 part of chloride of lime be added to 8 parts of olive oil, the latter, if pure, separates completely into two layers at the end of four or five hours, the temperature being from 17° to 18°; but if it is mixed with an eighth or more of poppy oil, the separation is incomplete, and takes place with extreme slowness. According to M. Lailler, every olive oil must be considered false which, when mixed with one-fourth of its weight of chromic acid, does not at the end of twenty-four hours present a perfectly opaque liquid. According to Chevallier, in one part of France the oil is sophisticated with honey, an adulteration not likely to take place in England. It is easily discovered, for the oil has only to be shaken up with water, and the water separated and submitted to the usual tests for sugar.

PART IX.—EXAMINATION AND ANALYSIS OF WATER.

§ 316. Pure water neither exists in nature nor even in the laboratory of the chemist, save on those rare occasions when, with immense expenditure of time and labour, water is purified either by repeated distillation over permanganates in a vacuum, or made synthetically. Nevertheless, however difficult it is to obtain even an ounce of water which shall consist of 1 part of hydrogen and 8 parts of oxygen by weight, and no other admixture, it may yet be very easily obtained sufficiently pure to warrant the epithet "pure" water—*i.e.*, containing impurities only to be detected by reagents of great sensibility, or, what amounts to the same thing, by operating on a large quantity of water. In the analysis of water, therefore, it need scarcely be added that it is not the water *per se* which the chemist really analyses; but his researches are directed with the object of unveiling and determining the nature, and where possible the amount, of whatever may be present, foreign to water, whether in suspension or solution, whether of mineral origin or as one of the myriad forms of "life." The experimental and analytical methods in use mainly fall under the following divisions—

I. Examination by the Senses.—Smell, Sense of Taste, and General Appearance.
II. Physical Examination.
III. Chemical Methods.
IV. Biological.—Embracing A, microscopical appearances; B, cultivation of fungi and dormant germs; C, experiments on animals and human beings; D, experiments on fish.

I. Examination by the Senses.

§ 317. Water that is evidently turbid, that possesses an odour and an unpleasant taste, *requires no analytical processes to condemn it entirely; such a water is unsuitable for drinking purposes.* A water that even possesses any one of the enumerated bad qualities will, as a rule, be found to hold in solution sufficient impurities to make it decidedly objectionable. Most drinking-waters when looked at, or tasted, or smelt, without special precautions, have neither colour nor odour; on the other hand, all water, if viewed through a sufficiently deep stratum, possesses colour.

Colour.—To ascertain the colour of water, it is usual for analysts

to be provided with a colourless glass tube, at least 2 feet in length, having the ends closed with plate glass, and a small opening in the side of the tube through which to pour the water. A cheaper method of securing an aperture through which to introduce the water is to have a segment cut out of one of the glass discs, or a segmental section out of the end of the tube itself; the most convenient diameter of the tube is 2 inches, but one greater or smaller will answer the purpose. To make an observation, the tube is half-filled with the water to be examined, and then directed towards a white surface, which may be a white cloud in the sky or an equally illuminated sheet of paper. The air-filled space above the water then affords an excellent semi-circular disc of comparison, and renders it easy to detect the slightest shade of colour. The purest waters have the slightest tinge of blue; the next in order of purity have a just distinguishable shade of green. Decided green tints, London fog hues, amber yellow, and brown tints are those possessed by waters tinged with peat, containing suspended matters, of second class composition, or those of considerable impurity.*

Smell.—Half a litre of the water or more is warmed in a large corked or stoppered flask to 38° [100° F.]; a long glass tube of three-quarters of an inch in diameter is now inserted, and the water sucked up once or twice so as to wet the side of the tube thoroughly; then, without taking the tube out of the flask, one nostril is applied to the orifice of the tube, the other closed by the finger, and deep inspirations or "sniffs" taken.

Another simpler plan is to warm a quantity of the water, without removing the stopper, up to the temperature given, then shake, remove the stopper, and smell; a putrid odour denotes decomposing animal or vegetable matter. If the sample is much polluted by fresh sewage, a urinous odour is not unfrequently distinct. But, again, it may be specially noted that water quite unfit to drink may have no odour, hence the usefulness of the test is limited. A positive smell teaches volumes—a negative result is of little value.

Taste.—A few waters, and a few only, have a decided taste. It is scarcely to be recommended that analysts should taste samples derived from fever-stricken localities; but, on the other hand, when there is no suspicion of the samples having been the

* Messrs. Crookes, Odling, and Tidy, in their report on the London waters supply for 1881, describe an ingenious "colour meter," consisting of two hollow wedges filled, one with a brown and the other with a blue solution. Any desired combination of green and blue may be made by sliding the wedges across each other in front of a circular aperture in a sheet of metal, and thus imitating the tint of water under examination; each prism is graduated from 1 to 50, the figures representing millimètres of the thickness at that particular part of the prism.

cause of any illness, the palate may detect some not unimportant peculiarity.

II. Physical Examination.

§ 318. The physical examination is mainly microscopical. Dr. W. Russell and W. Laplace* have recently discovered, it is true, that with a column of pure water 6 feet in length there is a distinct single absorption-band; and hence it is probable that, at all events, waters containing desmids and green vegetable cells generally would show particular spectra, but this has not yet been worked out; it will be more convenient for our purpose to consider the microscopical appearances later. (See p. 340.)

III. Chemical Methods.

§ 319. A complete examination by chemical processes embraces the following determinations :—

1. Total solid residue.
2. Estimation of the halogens, chlorine, and occasionally iodine, and in a few cases bromine.
3. Phosphates.
4. Nitrates and Nitrites.
5. Sulphates.
6. Oxygen consumed in the Forchammer process.
7. Free and albuminoid ammonia.
8. Hardness.
9. Alkalinity.
10. Organic Analysis — Estimation of organic carbon and nitrogen.
11. Mineral analysis of water.

The ordinary analyses, sufficient in most cases to pronounce an opinion as to the fitness of a water for drinking purposes, embrace only 1, 2, 3, 4, 6, 7, and 8.

1. *Total Solid Residue.*—By the total solid residue of a water is meant the substances in solution, as determined by drying up a measured portion, and weighing the dried residue; if the water contain suspended matters, it should first be filtered, and a portion of the clear filtered liquid taken. The amount suitable for this determination depends upon the characters of the water. The soft Devon waters yield a very insignificant residue from 100 cc., and to obtain trustworthy results, at least a quarter of a litre is required; while, on the other hand, with calcareous waters, good results may be always obtained from 100 cc. With waters the characters of which are unknown, it will be best to operate on

* *Journal of the Chemical Society.* April, 1881.

a quarter of a litre, or (if working with English measures) one-twentieth of a gallon. The water may be placed in a platinum dish, and evaporated down to a small quantity over a ring burner, taking care that the liquid in no case boils or even simmers; the last drops are driven off on the water-bath. It is recommended by the Society of Analysts to heat the residue up to 104°·4(220°F.) in the air-bath, and then to cool under a desiccator; but with waters of unknown composition, it will be best to weigh the residue, which has not been exposed to a greater heat than 100°, for it is always open to the chemist to expose the residue thus obtained to higher temperatures. The examination of the solid matters by the eye will often not unfrequently reveal much. Iron gives a coppery lustre to the dish, manganese a green to the ash, and very pure waters leave a residue almost white. The dish with its contents is next heated to a low redness, by the aid of a good Bunsen's burner, furnished with a rose, and then cooled and weighed. Note should be taken of any blackening or scintillation. The dish is again cooled and weighed, the loss of weight being returned as loss on ignition, and this final residue is dissolved in the manner to be described, and used for the qualitative determination of the phosphates.

2. *Estimation of the Halogens.*—The estimation of chlorine is an essential part of the ordinary scheme of water analysis; that of iodine is rarely (perhaps too rarely) performed, while so few waters contain an estimable amount of bromine, that it need not be here described.

Chlorine.—Chlorine exists in ordinary waters in the form of sodic chloride, and occasionally a small portion of the total chlorine is combined with potassium. It is always estimated volumetrically by a standard solution of silver-nitrate (See *Appendix*), using as an indicator neutral potassic chromate. Nitrate of silver in presence of potassic chromate and alkaline chlorides (when the solution is neutral) first uses up or decomposes all the chlorides, and then attacks the chromates. Chloride of silver being white, and chromate of silver being red, the formation of silver chromate is indicated immediately by a red colour. At least 100 cc. of ordinary water (or, if grains are worked with, 140 grains) are to be taken for the determination of chlorine. With much-polluted waters, with those near the seashore or other places in which the ground is impregnated with salt, such a quantity may be inconvenient, and it will be necessary then to dilute with distilled water, taking of the diluted liquid a known quantity. In any case, the water is put into either a white porcelain dish or a beaker standing on a white slab. 1 cc. of the chromate solution (or 15 grains) is added to the water, and

the standard solution run in from a graduated burette or pipette. The exact termination of the process is best observed through a glass cell, in which a little pale chromate solution has been placed. Since the eye, looking thus through yellow light, is very sensitive to the red rays, it may be necessary—especially where great accuracy is required—to repeat the determination in the following way. The water from which the red colour of the silver chromate cannot be discharged by stirring, is rendered again whitish-yellow, by the cautious addition of a very dilute solution of common salt. A fresh portion of water is titrated in a fresh dish or beaker, side by side with the former; in this way the first permanent difference of colour can be observed. The results may be expressed in chlorine as chlorides, or it may be returned as common salt; the chlorine found may be multiplied by the factor 1·648, or more exactly by 1·64788. The following short table may facilitate calculation :—

Chlorine.	Sodium Chloride
1·	1·648
2·	3·296
3·	4·944
4·	6·592
5·	8·240
6·	9·888
7·	11·536
8·	13·184
9·	14·832
10·	16·480

Iodine.—M. Chatin* has upheld the theory, that goitre is caused by waters insufficiently iodised—a proposition which cannot be considered proved. However, although M. Chatin has failed to convince the scientific world of the truth of his theory, he has done good service in showing how easy the detection and estimation of iodine in water really is, and in demonstrating the fact that most waters contain it in appreciable quantity. The process which M. Chatin used in his researches was: To evaporate one or two litres of the water to dryness with pure potassic carbonate, to calcine very moderately this dry residue, and then to extract with strong alcohol of 94 per cent. This alcoholic solution is again evaporated to dryness, and moderately calcined; the last residue is dissolved in a very little water, and will show all the reactions of potassic iodide. It is colorimetrically estimated by palladium. A solution of chloride of palladium gives a distinct colour with an infinitesimal quantity of iodine; hence it is only necessary to have a standard solution of potassic iodide, containing say 1 milligramme in 100 cc., and to estimate it precisely on the same principles as detailed (page 526) for ammonia. Mr. Marchand,† pursuing the same line of researches, has preferred to precipitate from ten to twenty litres with nitrate of silver, collect the precipitate which may contain the chloride, iodide and bromide of silver, and dissolve it in sodic hyposulphite. The silver is now thrown out of this solution by sulphuretted hydrogen, and the solution, when freed from

* *Compt. Rend.*, t. xxxv., xxxix. † *Compt. Rend.*, xxxv.

silver sulphide, evaporated to dryness with a little hydropotassic carbonate. In this way he obtains the chloride, bromide, and iodide of potassium. When the residue is perfectly dry, it is extracted with strong alcohol of 85 per cent.; the alcoholic liquid is evaporated to dryness at a temperature not exceeding 75°. This last residue is again taken up by alcohol, and treated similarly to the potassic iodide obtained by Chatin's method.

3. *Phosphates.*—The residue after ignition is treated with a very little nitric acid, and evaporated to dryness; this treatment renders the silica insoluble. It is now again dissolved in a few drops of nitric acid, some water added, and filtered through an exhausted filter. If the filtrate is more than 5 cc., it should be concentrated to a smaller bulk, and its own volume of the molybdic solution added. The solution thus treated, and gently warmed, gives a more or less deep colour or a decided precipitate, according to the amount of phosphoric acid present. It may be estimated colorimetrically by a known solution of sodic phosphate, but this with no great accuracy. To make a gravimetric estimation of phosphates, save in polluted waters, may require several litres, and will seldom repay the trouble. Hence phosphates may be returned in a qualitative manner as "*traces,*" with a feeble colour; "*decided evidence*" with a darker colour, and as "*estimable amount*" if there should be a precipitate. The Analyst Committee have adopted "*traces,*" "*heavy traces,*" and "*very heavy traces,*" as expressing three degrees of phosphate contamination. Such phrases are convenient, though somewhat paradoxical, and the author therefore prefers the more logical form of expression given above.

4. *Estimation of Nitrates.*—The several methods in use for the estimation of nitrates may be arranged under three heads:—

(1.) Estimation of nitrates by conversion of the nitrate into ammonia.

(2.) Estimation of nitrates by decomposing the nitrate into nitric oxide, and measuring the gas.

(3.) Indirect estimation by means of indigo.

(1.) *Estimation as Ammonia.*—The most convenient method of obtaining the nitrogen of nitrites and nitrates in the form of ammonia is decidedly by the aid of the "copper-zinc couple." This method was first proposed by Gladstone and Tribe, and afterwards worked out in detail by Mr. M. Whitley Williams.* It appears that the copper-zinc couple decomposes nitrates first into nitrites, and then the nitrites into ammonia; nitrites are present to the last, and when all the nitrites have disappeared, it is certain the conversion into ammonia is complete. A low tem-

* *Journal of Chemical Society*, March, 1881.

perature, alkalies, alkaline earths and their carbonates, retard the reaction, while carbon dioxide, all acids, mineral acids, oxalic, phosphoric and common salt, as well as elevation of temperature, increase the reaction. In practice, a temperature of 24° is recommended as easily attainable.

Manufacture of the Copper-Zinc Couple.—Pieces of clean zinc-foil, about 3 inches by 2 inches, are immersed in a 3 per cent. solution of cupric sulphate, the zinc rapidly becomes coated with metallic-copper. When a sufficient coating is obtained, the solution is poured off, and the couple well washed with water, finally drained, and the water for analysis poured on to the couple. It is best to do these processes in one and the same stoppered bottle. The water may nearly fill the bottle, and the stopper may be inserted, for there will be no gas evolved until the nitrates are entirely decomposed. The water thus treated is put in a warm place, and if the action is allowed to go on all night, the ammonia will be ready for estimation in the morning. The quantity to be taken for the estimation of nitrates according to this plan, may be a quarter of a litre, or, if English measures are used, say 5 ounces. To very hard waters the addition of a little oxalic acid is recommended. In any case where there is doubt whether the conversion into ammonia is complete, Griess's test, to be mentioned further on, should be used; and if there is evidence of nitrous acid, the water must be left for a longer period. If the water possesses colour interfering with the Nessler agent, or matters precipitated by Nessler, it must be distilled in the ordinary way, and the ammonia estimated in a fractional part of the much-diluted distillate. In most cases this is unnecessary, and by taking a measured quantity of the water and diluting it considerably, a fairly correct colorimetric estimation can be made by the direct addition of the Nessler reagent to the water thus diluted. It will be necessary to subtract from the amount of ammonia found, that which has been determined to exist in the water as ammonia. The ammonia derived from nitrates and nitrites must be expressed either as nitrogen or as nitric acid.

The Aluminium Process.—The metal aluminium, when acted on by a caustic alkaline solution, decomposes nitrates into ammonia. A solution of soda of about 10 per cent. is prepared perfectly free from nitrates, by dissolving bit by bit metallic sodium in water. Any convenient quantity (such, *e.g.*, as 100 cc., or 2,000 grains) of the water is placed in a suitable retort, which is fitted in an air-tight manner to a condenser, terminating in a flask as in the arrangement figured at page 378. An equal quantity of the soda solution is added, and the whole boiled until

free from ammonia; the retort is cooled, and the aluminium-foil dropped into the liquid, the whole is left over-night, and in the morning heat is applied to the retort, and the ammonia distilled over, and estimated in the usual way.

(2.) *Estimation of Nitrates as Nitric Oxide—Crum Process.*—This is, perhaps, of all methods the most accurate, and it can be recommended to those who possess a suitable gas apparatus in perfect working-order, or a Lunge's nitrometer. The principle on which the method is based, is the fact that strong sulphuric acid, acting on nitrates or nitrites in the presence of mercury, decomposes the nitrates or nitrites, and the whole of the nitrogen is evolved in the form of nitric oxide. The details of the process are briefly as follows:—It is absolutely necessary, for the application of the test, that the nitrates be in concentrated solution; hence the nitrates must be extracted with as small a quantity as possible of hot distilled water, from the dry residue of half a litre, or any other convenient quantity, according to the nature of the water. The author recommends, previous to this determination, a rough indigo assay of the amount of nitrates, which is useful as a guide. The hot-water extract (which contains nitrates, nitrites, if present, and chlorides)* is evaporated down to about 1 cc., and the liquid transferred to the decomposition tube, which is a short tube about 3 inches long, constricted at one end, and furnished with a cup and stopcock; open at the other, and having a bore easily closed with the thumb. This tube is filled with mercury, inverted, and clamped in a mercury trough with the cup uppermost; it is now easy to transfer the solution of nitrates by pouring the solution into the cup, and cautiously opening the stopcock. The vessel in which the filtrate has been concentrated is then rinsed into the cup with pure strong sulphuric acid, and ultimately one and a half times the volume of the concentrated nitrate solution of strong sulphuric acid is worked into the tube by opening carefully the stopcock. No air must be allowed to gain admittance. Should gas be immediately evolved, it is carbonic dioxide, and must be got rid of, for nitric oxide is not at once evolved. On the mixture of sulphuric acid and nitrate having been transferred into the tube, the lower end is closed by the thumb, and the tube shaken so as to mix up the acid and the mercury, when the gas in a short time begins to come off, and considerable pressure may have to be exerted. When the reaction is complete, the contents are transferred to any gas apparatus and measured. Every two volumes of nitric oxide

* It was at first considered necessary to remove chlorides by silver sulphate, but Mr. Warrington's experiments have shown this to be unnecessary.

equals one volume of nitrogen. The weight of the nitrogen is obtained from Table LVII. (p. 557).

(3.) *Indigo Process.*—This process is based on the decolourisation of indigo when nitrates or nitrites are decomposed by strong sulphuric acid.

When certain kinds of organic matter are present, the results are entirely without value. On the other hand, with careful working, the test is correct with the great majority of waters, and as a means of rapidly determining the nitrates in unknown samples, with a view to their determination by other more exact processes, it is very useful. Four grms. of sublimed indigotin are digested for some hours with five times their weight of Nordhausen oil of vitriol; the liquid is diluted with water, filtered, and brought to the volume of 2 litres.* A normal nitre solution is made by dissolving 1·011 grm. of pure potassic nitrate in one litre of water. From this solution, solutions of $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$, and $\frac{1}{64}$, normal are prepared. An assay is now made by mixing, say 20 cc. of the nitre solution with any amount of the indigo solution deemed sufficient, in a wide-mouthed flask of 150 cc. capacity. Oil of vitriol is run into a test-tube, the volume being equal to the united volumes of the indigo and nitre. The contents of the test-tube are then suddenly tipped into the flask, and the flask transferred to a chloride of calcium bath maintained at 140°. If the solution of indigo is insufficient, the liquid will be suddenly decolourised; if it is too much, no bleaching will take place, the liquid still retaining its blue colour. In either case a fresh determination will be requisite, and by doubling or halving the amount of indigo for the next experiment, as the case may be, the operator will soon find the limits, and five or six experiments will standardise the solution. In every instance a quantity of sulphuric acid, equal to the united volumes of indigo and water, must be used; the indigo solution should be diluted so as to be about equal to the nitre solution. As it is found that the quantity of indigo consumed is not precisely in proportion to the nitric acid present, but diminishes as the nitrate solution becomes more dilute, the further standardising of the indigo solution by the more dilute solutions of nitre already alluded to is necessary. The results may be thrown into a table as follows. (See Table LIII., next page.)

The method of using the table is sufficiently obvious to those who are accustomed to calculations of the kind; supposing, for example, 20 cc. of the water used up 6·64 cc. of the indigo; this is ·5 cc. above the nearest number in the table, viz., 6·14. Now, taking

* See Mr. Warrington's excellent paper, *Journ. Chemical Society*, Sept., 1879, p. 579; also, Frankland's "Water Analysis," p. 31.

TABLE LIII.—VALUE OF INDIGO, IN NITROGEN, FOR DIFFERENT STRENGTHS OF NITRE SOLUTION.

Strength of Nitre Solution Used.	Indigo required.	Difference between Amounts of Indigo.	Nitrogen Corresponding to 1 cc. of Indigo.	Difference between the Nitrogen Values.	Difference in the Nitrogen Values for a Difference of 1 cc. in the Amount of Indigo.
	cc.	cc.			
$\frac{8}{64}$ normal, .	10·00	...	·000035000	...	...
$\frac{7}{64}$,, .	8·71	1·29	·000035161	·000000161	·000000125
$\frac{6}{64}$,, .	7·43	1·28	·000035330	·000000169	·000000132
$\frac{5}{64}$,, .	6·14	1·29	·000035627	·000000298	·000000231
$\frac{4}{64}$,, .	4·86	1·28	·000036008	·000000381	·000000298
$\frac{3}{64}$,, .	3·57	1·29	·000036764	·000000756	·000000586
$\frac{2}{64}$,, .	2·29	1·28	·000038209	·000001445	·000001129
$\frac{1}{64}$,, .	1·00	1·29	·000043750	·000005541	·000004295

the extreme right-hand column, the difference for the nitrogen values of 1 cc. will be found; and as there is in this case a difference of only half that quantity, halving the number gives us ·000000115; this number has to be subtracted from the unit value of nitrogen found in the first column, thus:—

$$·000035627 - ·000000115 = ·000035512,$$

which is the nitrogen-value of each cc. of the indigo. Hence, as we have supposed that 20 cc. of the water decolourised 6·64 cc. of indigo, the nitrogen as nitric acid in parts per 100,000 is 1·179, or in grains per gallon ·82 grain. If the indigo estimation of nitric acid is only a preliminary step to a further and more exact determination by the Crum method, these refinements are not necessary. The indigo solution is standardised once for all by the normal solution of nitre, and if the nitrates are either very large or very small, an allowance is made.

Nitrites.—However important the detection qualitatively of nitrites may be, it is seldom necessary to determine them quantitatively; but when this is required it would appear that the reaction between nitrous acid and meta-phenylenediamine, first proposed by Peter Griess, and since elaborated by Preusse and Tiemann, affords the readiest method both of detection and estimation. Meta-phenylenediamine gives a red colour with nitrous acid, even in very dilute solution. It is so delicate a reagent as to be capable of detecting one part of nitrous acid in

30,000,000 parts of water. For the estimation of nitrates by this method, there will be required,—

(1.) A solution of 5 grms. of meta-phenylenediamine in one litre of water, and made acid with sulphuric acid.

(2.) Sulphuric acid, strength 35 per cent.

(3.) A solution of pure potassic nitrite, strength ·01 mgrm. of N_2O_3 in every cc. This is best made by dissolving ·406 of argentic nitrite in hot water, decomposing it with a slight excess of potassic chloride, allowing the silver chloride to settle, and then diluting each 100 cc. of the clear fluid again to a litre.

The actual operation is performed by putting 100 cc. of the water to be tested into a narrow glass cylinder, and adding first 1 cc. of the sulphuric acid, and then 1 cc. of the meta-phenylenediamine. If a red colour is immediately developed, less of the water must be taken, and it is to be diluted until the colour just shows itself at the end of one or two minutes. The colour thus obtained is imitated as exactly as possible by running from a burette a small quantity of the standard nitrite solution into a similar cylinder, adding a similar quantity of sulphuric acid and the meta-phenylenediamine; in short, the operation is precisely akin to "*Nesslerising.*" It must, however, be remembered that the nitrite solutions thus treated are continually getting darker, so that the final determination must be started simultaneously, and the final shade observed in both at the end of the same interval of time, which, as the reaction is somewhat slow, may be at the end of from twenty to twenty-five minutes.

5. *Sulphates.*—Any convenient quantity of the water, carefully measured, is acidified with hydrochloric acid, and heated nearly to boiling; while hot, some solution of chloride of barium is added, so as to be in slight excess, and the solution kept near the boiling point for some time. The sulphate of barium is allowed to settle, collected on a filter, dried, ignited, and weighed; one part of baric sulphate equals ·134335 of sulphuric acid.

6. *The Forchammer, Oxygen or Permanganate Process.*—The principle of this process is the abstraction of oxygen by the organic elements of the water, and the estimation of the oxygen thus abstracted. ·395 grm. of potassic permanganate is dissolved in a litre of water, which gives a solution containing 1 mgrm. in every 10 cc., or, if working in grains and septems, 2 grains of permanganate in 1,000 septems of water, equalling ·01 grain of available oxygen in 20 septems. This is the standard solution.

The determination is now usually made, as recommended by the Society of Analysts, in two stages, on two equal quantities of water, viz.—(1.) The amount of oxygen absorbed in fifteen

minutes, and commonly due to nitrites, or, at all events, substances very readily oxidisable; and, (2.) the amount of oxygen absorbed in four hours. The time for this last determination used to be given as three hours, but the four-hours period is preferable; and even then it is easy of proof that, if the water be allowed to stand, there still remain matters capable of being oxidised. The temperature is an important factor, for numerous experiments have shown that the amount of oxygen consumed varies greatly at different temperatures. The Analysts' Society have adopted 26°·6 (30° Fahr.), and in order to ensure uniformity this temperature is here recommended. It is, however, probable that better and more uniform results would be attained by boiling the water and permanganate for an hour. In some interesting experiments by Messrs. Wigner and Harland,* river water, to which a known quantity of pure sugar had been added, was found to have absorbed more oxygen at the end of two hours, at 37°·7 (100° Fahr.), than during six hours at 15°·5 (60° Fahr.), and almost as much as during six hours at 26°·6 (80° Fahr.) Similarly, river water contaminated by a known quantity of urine used up equal quantities of oxygen when acted upon by permanganate for six hours at 26°·6 (80° Fahr.), as it did when the process was accomplished in two hours at 37°·7 (100° Fahr.) The actual operation is as follows:—

Two stoppered flasks are taken, and a quarter of a litre of the water put in each [or 3,500 grains]. The bottles, with their contents, are immersed in an air-bath until the temperature rises to 26°·6 (80° Fahr.), then 10 cc. [or. 100 grains] of dilute sulphuric acid [1 : 3] are added, and the same quantity of the standard permanganate. One of the bottles is taken out at the end of a quarter of an hour, and two or three drops of potassium iodide added to remove the pink colour. After thorough admixture, there is run into it from a burette a solution of sodium hyposulphite, the value of which has been determined by titrating 10 cc. of the standard potassium permanganate in distilled water until the yellow colour is nearly destroyed; then a few drops of starch water are added, and the hyposulphite added until the blue colour is just discharged. At the end of four hours the other bottle is removed and titrated in exactly the same way. Should the pink colour diminish very rapidly during the four hours, another measured quantity of permanganate must be added.

If A be taken to express the amount of hyposulphite used for a blank experiment with pure distilled water, B the water

* On the Action of Permanganate on Potable Waters at Different Temperatures. *Analyst*, March, 1881, p. 39.

under examination, and a the amount of available oxygen in the quantity of permanganate originally added: then, the oxygen consumed by the quantity of water operated on would be

$$\frac{(A - B)a}{A}$$

or, in actual figures, 10 cc. of a permanganate solution, equivalent to ·001 grm. of oxygen, were added to a quarter of a litre of distilled water, and to the same quantity of a sample under analysis. The distilled water used 40 cc. of hyposulphite, the water 15 cc. at the end of four hours. Then the oxygen consumed by the quarter litre was 000625, according to the equation

$$\frac{40 - 15 \times \cdot 001}{40} = \cdot 000625$$

or per litre, ·0025 [·175 grain per gallon].

7. *Ammonia, Free and Albuminoid.*—The estimation of ammonia depends on the principle that it admits of ready distillation when it exists in the water as ammonia, provided that the water is alkaline. Since, therefore, nearly every natural water is alkaline, distillation of water is alone sufficient to expel the ammonia. If a water, by testing with cochineal, is found to be acid, then it will be necessary to add a little recently ignited carbonate of soda (or, perhaps better, a little recently burnt magnesia), until an alkaline reaction is obtained. The apparatus required for the estimation of free and albuminoid ammonia, is—

(1.) A good large stoppered retort, fitting into a full-sized Liebig's condenser, through which a constant stream of water is running.

(2.) Measuring-flasks, either in septems or litres.

(3.) Cylinders made of clear glass, "Nessler cylinders."

(4.) One or two pipettes.

(5.) Nessler reagent (*see Appendix*, p. 553).

(6.) Standard solution of ammonium chloride (*see Appendix*, p. 553.)

(7.) Solution of alkaline permanganate (*see Appendix*, p. 553.)

The water is first tested with a little of the Nessler reagent; if it shows any decided colour it may be necessary to distil a very small portion, say a quarter of a litre, diluted with a sufficient quantity of pure, ammonia-free water. But if, on the other hand, there is no colour, or a doubtful one, a litre of the water should be distilled, or a fifth of a gallon. On distillation, 100 cc., or 1400 grains, are collected in one of the glass cylinders, and 5 cc., or one-twentieth of its volume, of clear straw-coloured Nessler solution added. If there is any ammonia the distillate thus

tested will be tinted or coloured, the colour varying from a very pale straw up to a dark amber. If the colour should be very deep, it is impossible to estimate the ammonia with even an approach to accuracy, unless the dark solution is very much diluted and made up to definite volumes, of which definite volumes fractional parts are taken. The next step is to estimate the ammonia by imitating the colour. This is done by running into some distilled water one, two, or more cc.'s of the standard ammonium chloride solution, and adding exactly the same amount of Nessler solution as had been added to the distillate. The solution is now made up to precisely the same bulk as the distillate, and the liquids, thus in equal columns, compared by looking down through them on to a glass plate or white porcelain tile or slab.

It is important to compare the solutions at the same period of time, for there is a slow darkening of colour, partly dependent on absorption of ammonia from the atmosphere, and partly due to the completion of the reaction. If the colour does not agree, a second, third, and fourth trial is made. These trials may be much shortened by pouring off a certain quantity of the darker liquid until the shortened column has the same tint as the longer column, and then confirming the result thus obtained by an actual trial. Thus, 5 cc. of ammonium chloride, equalling ·05 milligrammes ammonia, were found, when tested in 100 cc. of water with 5 cc. of Nessler, to give too dark a colour. Hence the ammonia in the distillate was less than ·05 mgrm. What quantity would it probably contain? The Nessler cylinders were graduated into parts, and on pouring off a certain quantity of the darker solution, until the columns were equal in colour, the one column was 67 parts high, the other 80. Hence, if 80 parts were equal to ·05 mrgm. of ammonia, 67 must be equal to ·042; and it is only necessary to test the correctness of this by a second determination, using this time about 4 cc. of the standard solution.

By graduated Nessler glasses, having taps near the bottom in order to run off a portion, as well as by colorimeters, such as Mill's and other like contrivances, "Nesslerising" is much expedited and facilitated. Nevertheless, it is not a very accurate method of estimating ammonia. The verdict must be useful and comparative, not accurate. The accuracy of colorimetric estimations of ammonia depends upon the practice of the observer, and the sensitiveness of his eye for differences of colour. There are many persons who, from some physical peculiarity of sight, can only distinguish a few shades, and even with the greatest care can make no very accurate colorimetric observation.

Returning to the actual estimation of free ammonia, the water

must be distilled in successive fractions, until no more free ammonia is detected in the distillate. This occurs generally when 150 cc. or 200 cc. (that is, one-fifth of the entire quantity) of the water taken has come over, then the water is ammonia-free. The next step is to estimate in the same water the albuminoid ammonia.

Albuminoid Ammonia.—When Mr. Wanklyn published first the albuminoid process it was very generally adopted, and it may be considered as yielding quickly certain data, assisting in the final verdict of an analyst. To the water about one-tenth of its original volume of the alkaline permanganate (*see Appendix*, p. 553) is added; the water is again distilled; successive fractions of the distillate are tested with Nessler, and the ammonia therein contained determined in the same way as in the free ammonia estimation. Here the analyst often has considerable difficulty, from the circumstance that evidently the alkaline permanganate often sets free certain compound ammonias, which strike a tint with the Nessler re-agent entirely different from that given by pure ammonia. In certain cases it may, indeed, be necessary to estimate the ammonia by titrating with a feeble and very dilute acid. The free ammonia is usually returned as ammonia; the albuminoid should properly be returned as "*nitrogen as albuminoid ammonia.*" It is scarcely necessary to remind the operator that all retorts, condensers, &c., used for these estimations must be ammonia-free, and that ammonia from any analytical operation must not be allowed to contaminate the laboratory atmosphere. The most ready way to render it certain that there is no ammonia in the condenser is to acidify a little water with sulphuric acid, and then distil until the distillate is ammonia-free.

8. *Hardness.*—A. *Before Boiling.*—In a corked or stoppered bottle 1000 grains, or 100 cc., of the water to be tested are placed. The standard soap solution (*see Appendix*, p. 553) is run in, 10 grains, or 1 cc., at a time, and after each addition the cork or stopper is replaced, and the bottle shaken violently, and observed as to whether a permanent lather forms or not. If not, then another measured quantity is run in, and so on until the desired effect is produced. Waters containing but little magnesia give a good lather, and the reaction is fairly sharp. With magnesian waters the reaction is slow, and not so easy to observe. When a lather has been obtained, it is well to repeat the experiment, and in this second assay to run in within half a division the whole of the amount of soap solution thought to be necessary; then a further portion of the soap solution is run in very gradually in tenths of a cc., or single grains, until the lather is permanent. The hardness is expressed in degrees. However, when the hardness is more than 16°, it is not possible to estimate it in this

way with accuracy, and the water under examination must be diluted with distilled water to double its bulk, and then the same quantity as above recommended taken for the estimation: in this case the number of degrees found must, of course, be multiplied by 2.

B. *Hardness after Boiling.*—A quantity of water, precisely the same in bulk as in the former experiment, is boiled briskly for half-an-hour, and made up to the original bulk with distilled water; filtered, cooled, and treated with soap solution, exactly in the same way as in the previous case.

9. *Alkalinity.*—The alkalinity of water is best taken by using as an indicator an alcoholic solution of tincture of cochineal, which is not affected by carbonic acid, and strikes a beautiful crimson purple colour with a trace of alkali, a reddish-yellow with acids. 100 cc. or more are placed in a tall cylinder of colourless glass, and a decinormal hydrochloric acid is run in, drop by drop, from a burette until the colour changes to a yellowish hue. The result is expressed in terms of carbonate of lime, each cc. of decinormal acid equalling 5 mgrm. of carbonate of lime.

10. *Organic Analysis of Water: Estimation of Organic Carbon and Nitrogen.*—(1.) *Carbon.*—There are four main ways in which the carbon in a water residue is estimated—(1.) as gas; (2.) gravimetrically; (3.) nephelometrically; (4.) indirect methods.

(1.) *Carbon as Gas.*—The first method (which consists in burning up the carbon into carbon-dioxide, and estimating both it and the nitrogen in a suitable gas-apparatus) we owe to Dr. Frankland, who proposed and practised it as early as 1867.

Frankland's Combustion Process.—A quantity of water, varying from 100 cc. to a litre, according to the amount of impurity suspected from other determinations [especially of the free ammonia] is evaporated to dryness with special precautions. These precautions are mainly two—(1.) The protection of the sample from dust during the evaporating process, and (2.) the destruction of carbonates, nitrates, and nitrites, which, it is scarcely necessary to say, would greatly interfere with the results, and indeed render them valueless. Small quantities of water, such as sewage and the like, can be evaporated under any improvised cover, but for larger quantities Dr. Frankland recommends a self-filling circular water-bath, on the top of which rests a flanged copper capsule, serving as support to a thin glass dish, in which the evaporation of the water takes place. The dish is protected from dust by being covered by a tall glass shade, such as is used for statuettes. The bulk of the water for evaporation is contained in a flask, to the neck of which is a ground glass tube bent appropriately. The flask, when filled with the water and connected

with this tube, is by a quick movement inverted, so that the end of the tube rests on the glass dish. A little above the end of the tube there is a short side tube bent at right angles, of smaller diameter than the tube itself, the effect of which is that directly the water in the dish falls below the little angle of this tube, air bubbles up into the flask, and more water runs into the dish. In this way the evaporating dish is kept at a constant level until the whole of the water is used up. The steam condenses on the inside of the glass shade, and collects in the copper capsule underneath the glass dish, and is finally conducted away by a piece of tape which passes over the copper lip of the bath. The evaporation of a litre of water takes about 26 hours, but with proper arrangements it is continuous, and when once started requires no supervision. The evaporating time is really a small matter, for the analyst can begin it one morning, and it will be ready the next. Before the water is submitted to evaporation it is boiled briskly with 20 cc. of sulphurous acid; or if previous estimations have shown that there is a larger quantity of nitrogen as nitrates and nitrites than ·5 per 100,000, a larger amount of sulphurous acid must be added. To ensure the destruction of nitrates, a drop of ferrous chloride is added to the first dishful of water. Lastly, in dealing with waters deficient in carbonates (in which case the sulphurous acid, when oxidised to sulphuric, might not offer a sufficient base for combination, and therefore there might be some destruction of the organic matter), 1 or 2 cc. of a saturated solution of hydric sodic sulphite are added, which will give any sulphuric acid, otherwise free, sufficient base for combination. When the evaporation is complete, the next step is to remove the residue from the dish and burn it up in a vacuum with oxide of copper. To avoid this removal, Dr. Dupré has proposed and used a collapsable silver dish: the water in this dish is evaporated down in the usual way, and then the dish can be rolled up and thrust into a combustion tube. If the analyst does not use the silver dish, the residue must be removed by the aid of a flexible spatula, and mixed with copper oxide. The combustion tube, 18 inches long and of rather narrow bore, is cleansed and dried, and charged by the aid of a small metallic scoop, first with a little coarse oxide, after which the residue is mixed with oxide; lastly some more oxide is added, and in front of this is placed a roll of copper gauze which has first been oxidised in air and then reduced in hydrogen.

The usual precautions in filling a combustion tube for organic analysis are, of course, to be strictly observed. The tube is now placed in a combustion furnace, exhausted of all air by a Sprengel pump, the tube made gradually red-hot, and the gas finally trans-

ferred to a gas apparatus. The present writer has forsaken the use of Sprengel pumps, and for this and all other vacuum operations employs the mercury pump described at page 70, the figure of which is here repeated. The combustion tube is attached by a short piece of pressure tubing direct to the bent tube at Z, made perfectly vacuous, and when no air is delivered into B the stopper, F, is replaced by the tube SS′P. After having filled the thread of SS′P with mercury, and again seen that there is no air in the apparatus, it should be left for a short time to ascertain whether the single joint is sound. Any leakage is discovered by the mercury column sinking in AA. All being sound, the point P is placed under any eudiometer or gas-apparatus which the analyst may have, and the combustion proceeded with, the gas finally being pumped into the measuring apparatus by opening the stopcock S′, and working the reservoir R up and down. There is no method superior to this, and few equal to it.

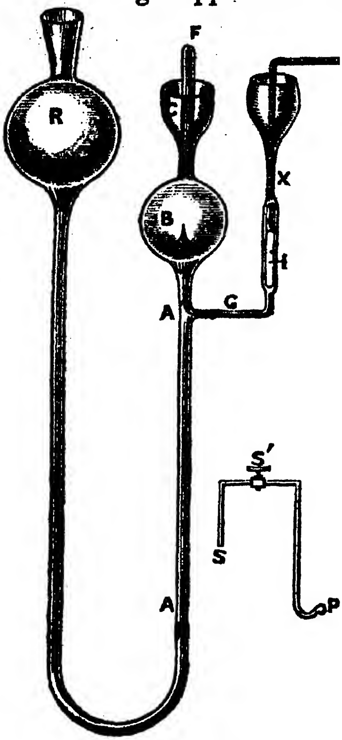

Fig. 46.

The author also uses a gas apparatus somewhat different from that generally employed. This apparatus consists (see fig. 47) of a reservoir, A, attached by an india-rubber pressure tube to a glass tube, B, which in its turn is connected with the steel block invented by Mr. J. W. Thomas.* The barometer tube, C, possesses no stopcock, it being unnecessary; but it is filled perfectly with mercury, and then stoppered with caoutchouc and a bit of glass rod, and finally sealed from any air-leakage by a little cell filled with mercury (S). The laboratory tube, V, is a glass cylinder of $\frac{1}{8}$ diameter and 5 in. in length, and provided with several divisions at equal distances. It is secured by a suitable clamp in the mercury trough [this clamp is omitted in the diagram], and when it is wished to connect it with the reservoir and barometer this is easily effected by slipping it on to the end of the

* *Journal of the Chem. Society*, May, 1879, p. 218.

tube, I, which is fitted securely and permanently into the bottom of the mercury trough, and has been ground so as to fit the end of the laboratory tube with a perfect yet easy joint. V is also jacketed, as indicated by dotted lines. The jacket is a short cylinder, closed at the top by a caoutchouc stopper, through which pass two tubes, the one connected with india-rubber tubing from the barometer jacket, the other connected with a waste pipe. There is no practical difference as to the particular course for the water to take. It may enter the top or the bottom of the jackets, but there must be a constantly running stream. It is necessary, first of all, to find the exact millimètre division of the barometer tube, which each division of V corresponds to, and this is effected by directing a low power telescope, or, as for that, a tube to each division provided with a spirit level. It is also necessary to know the exact capacity of V, which is obtained by filling it with water, and allowing air to gradually displace the water, weighing the different fractions of the displaced water at each division.

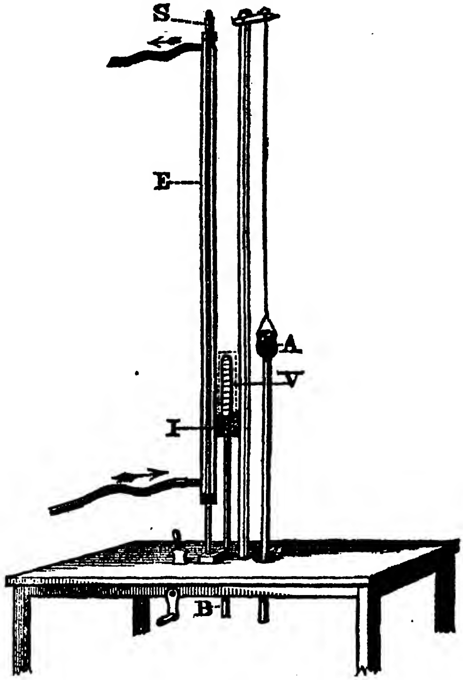

Fig. 47.

To make an ordinary analysis of a gas containing nitrogen and carbon dioxide, the gas is collected or transferred into V; V worked on to I; the reservoir lowered, after opening the way in the steel block, to both barometer tube and laboratory vessel, until any convenient division in V is reached (a good stream of water running all the time through the jackets); the height of the barometer tube is now read, the temperature of the water noted, and the usual calculations made. To absorb the carbon dioxide, V is carefully removed from off I, of course taking care in the removal that the open end of V is not lifted

above the mercury. A small bit of potash is now melted on to a platinum wire moistened and thrust up into the gas; it remains there until by shaking no further absorption is observed. The wire is then withdrawn, and V worked on to I as before, and the gas measured. If the laboratory vessel is furnished with platinum wires near the top, the apparatus can also be used for analyses by explosion. The writer prefers to absorb carbon dioxide in the old-fashioned way, by a piece of potash, so as not to soil the mercury too much by liquids; but when it becomes a question of the use of alkaline pyrogallic acid, or Nordhausen sulphuric acid, it is better not to use the laboratory vessel described, but to slip on to the end of I a small piece of rubber tubing, so as to make the large end of an ordinary burette fit mercury- and air-tight. The upper and smaller end of the burette is provided with good pressure tubing provided with a clamp, and by means of a bit of thick-walled capillary glass tubing connected with the pipette figured.

The pipette consists of two bulbs, A and B. C is a thick-walled glass tube, with a capillary bore; at X is the India-rubber connection. Before commencing an absorption, A must be filled through B with the reagent; it is then, when properly connected, easy to drive the gas over into A, and also at the last a thread of mercury sealing C. The pipette may now be disconnected and well shaken without any loss of gas, and absorption is far more rapid than when liquid reagents are applied in the ordinary manner. An analysis of a sample of air, and one of a gas consisting of carbon dioxide, nitric peroxide and nitrogen, may be cited as an example.

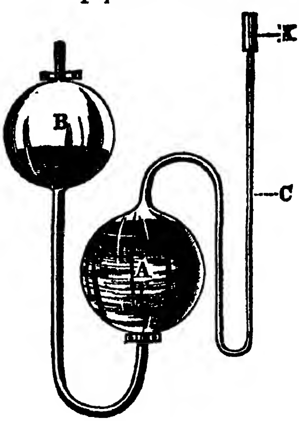

Fig. 48.

Air.—A sample of air brought to the tenth division of a burette fitted on to I, barometer tube reading 900 mm., but the barometer reading corresponding to division 10, is 325 mm. Therefore this has to be subtracted: 900 − 325 = 575 mm., which is the pressure of the total gas. On taking the burette off I, and inserting a moist stick of potash, and again reading at the same division, the barometer reading is now 899·8 mm.; this subtracted from 900 gives, as the tension of the carbon dioxide, ·2 mm. Lastly, on impelling the gas into the pipette (fig. 48), and submitting it to the action of alkaline pyrogallate for two

hours with frequent shaking, and measuring at the same division, the barometer reading is 780·9, which subtracted from the former reading gives as the pressure of the oxygen 119 mm. Hence

Pressure of carbon dioxide,	·2
,, oxygen,	119·0
,, nitrogen,	455·8
Total pressure,	575·0

Since the temperature was constant throughout, if the volume in percentages only is required, the calculation is as follows:—

(1.) 575 : ·2 : : 100 = carbon dioxide

$$\text{or } \frac{20{\cdot}0}{575} = {\cdot}03$$

(2.) 575 : 119·0 : : 100 = oxygen

$$\text{or } \frac{11900}{575} = 20{\cdot}69.$$

That is, the air contained ·03 per cent. of carbon dioxide, and 20·69 per cent. of oxygen.

In a determination of the carbon and nitrogen of a water residue (from a litre), the following is an example of the method and of the numbers obtained:—The gas was pumped out by the mercury-pump direct into V, V was then fitted on to I, and measured at the fourth division; the pressure of the mercury as read on the barometer tube was 850 mm.; but since the division itself equalled or corresponded to 284, the total pressure of the gas was 850 - 284 = 566 mm. On now absorbing by a stick of potash, the pressure was found to be 534, therefore the tension of the carbon dioxide was 850 - 584 = 266. Two bubbles of pure oxygen were now added, and the gas, which immediately became of a red colour, submitted to the action of alkaline pyrogallate; after this operation the barometer reading was 574, and therefore the pressure of the nitric peroxide was 584 - 574 = 10 mm. We have, therefore, the following determinations:—

Division 4 = 23·5 cc. Temp. = 11°·5

	mm.
Tension of nitrogen and nitric oxide,	300
,, nitrogen,	290
,, the three mixed gases,	566

These operations have furnished three uncorrected volumes of gases—

A. Volume of the three mixed gases.
B. Volume of nitric oxide and nitrogen.
C. Volume of nitrogen.

The volumes must, therefore, all be reduced by the usual calculations to 0° temp. and 760 mm. pressure.

From the corrected volumes the quantities of carbonic dioxide and nitrogen may be reduced as follows:—

$$A - B = \text{volume of } CO_2$$

$$\frac{B-C}{2} + C = \frac{B+C}{2} = \text{volume of nitrogen.}$$

From these corrected volumes of nitrogen and carbonic dioxide, the weights of carbon and nitrogen can be obtained by calculation or by tables. There is, however, a far simpler means of arriving at the desired result by the aid of the following data:—

1. The weights of carbon and nitrogen contained in equal volumes of carbon dioxide and nitrogen gases, measured at the standard temperature and pressure, are to each other as 3 : 7.

2. The weights of nitrogen contained in equal volumes of nitrogen and nitric oxide are as 2 : 1.

Hence, if we assume that for the purpose of calculation the gaseous mixture consists entirely of nitrogen, and that two successive portions of the nitrogen are removed from it by the reagents; then, if A be the weight of the total gas calculated as nitrogen, B the weight after absorption of the first portion (CO_2), and C the weight after the absorption of the second portion (N_2O_3); further, if x and y represent respectively the weights of carbon and nitrogen contained in the gaseous mixture, then the following simple equations express the values of x and y:—

$$x = \frac{3(A-B)}{7} \qquad y = \frac{C+B}{2}$$

In the example given the calculation is as follows:—

A.

Log. of div. 4 (23·5 cc.),	=	1·37106	
Log. of 566,	=	2·75281	
Log. from table LVII, p. 557, corresponding to 11°·5,	=	−6·20029	
		−2·32416	= ·02109

B.

Log. div. 4,	=	1·37106	
Log. of 300,	=	2·47712	
Log. from table LVII., p. 557, corresponding to 11°·5,	=	−6·20029	
		−2·04847	= ·01187

C.

Log. div. 4, ...	=	1·37106
Log. of 290, ...	=	2·46239
Log. from table LVII., p. 557, corresponding to 11°·5, ...	=	$\frac{-6·20029}{-2·03374} = ·01080$

$$\text{Carbon, ... } = \frac{3(·02109 - ·01187)}{7} = ·00438$$

$$\text{Nitrogen, ... } = \frac{·01187 + ·01080}{2} = ·01133$$

Or the water contains in 100,000 parts ·438 carbon, 1·133 nitrogen.

Other Methods of Determining Organic Elements.—Mr. Smethan* has published a process which does not entail the drying of the residue.

A litre of the water under examination is acidified with phosphoric acid, and concentrated to 50 cc. It is then oxidised by means of an oxidising mixture, consisting of 1 grm. of bichronate of potash, 1 grm. of permanganate of potash, and 20 cc. of sulphuric acid, of 1·4 specific gravity. The liquid is then boiled, and the CO_2 condensed in an absorption tube on similar principles to those adopted by Dupré and Hake, the carbonate of baryta being ultimately determined as sulphate. In Mr. Smethan's paper there are full details, and the test experiments with known weights of sugar, benzoic acid, isinglass, picric acid, and urea appear to be very satisfactory; but the writer has no personal experience of it.

In 1878 Messrs. J. A. Wanklyn and Cooper took out a patent† for a method of determining organic matter in water by means of an alkaline solution of permanganate of potash.

The solutions required for this patent process are:—

1. A solution of permanganate of potash, 1 cc. of which is equivalent to 1 milligramme of oxygen.
2. A solution of ferrous sulphate, 1 cc. of which exactly decolourises 1 cc. of the permanganate.
3. A solution of caustic potash (5 per cent).
4. Dilute sulphuric acid.

A litre, or any other convenient quantity of water, is placed in a clean retort; 5 cc. of the potash solution and 5 cc. of the permanganate solution are added, and the water is boiled until it measures about 700 cc.

If it decolourises during this process completely, another quantity of alkaline permanganate is dropped in.

After cooling, 10 cc. of the sulphuric acid and 5 cc. of the

* *Analyst*, Sept., 1880, p. 156. † 1878, Pat. No. 1504.

iron solution are added, which, of course, decolourise the liquid, and the standard solution of permanganate is next dropped in until a pink colour is produced.

The following may suffice as an example of the method of calculation :—A water was boiled in the manner detailed with 5 cc. of the permanganate and 5 cc. of the potash solution. On cooling, sulphuric acid and 5 cc. of ferrous sulphate were added; to restore the pink colour 4 cc. of the permanganate solution were required, hence the total permanganate used was the original 5 cc. and 4 cc. finally added—total, 9 cc. Subtract the 5 cc. of ferrous sulphate, which leaves 4 cc. of permanganate used by the impurities in the water, and as each cc. is equal to a milligramme of oxygen, it follows that the litre of water required 4 milligrammes of oxygen.

In a paper contributed to the *Philosophical Magazine*, Mr. Wanklyn has further developed the process, by stating that even acetates may be burnt up to carbonates, by raising the temperature of the alkaline permanganate to 160° or 180° with addition of a little hydrated binoxide of manganese to stop the evolution of oxygen.

There is no doubt of the powerful oxidising influence of alkaline permanganate, but hitherto few chemists, except the patentees, have used this process methodically in the examination of water, and there has been no general consensus of opinion with regard to its usefulness.

That the patentees can legally claim the invention of oxidation by alkaline permanganate as their own, seems a proposition hardly tenable, since it has been used before by various chemists; but its use in the particular manner laid down in the patent, and in the particular proportions given is, of course, a different matter.

Gravimetric Estimation of Minute Quantities of Carbon.—Drs. Dupré and Hake in 1879* published a method of gravimetrically estimating minute quantities of carbon by burning up in a current of pure oxygen, and then absorbing the CO_2 thus produced in baryta water, and converting the baryta carbonate into baric sulphate. A product was thus obtained which weighs 19·4 times as much as the carbon originally present.

The details of the process are as follows :—A combustion tube, open at both ends, and about 24 inches long, is drawn out and bent downwards at one end at an angle of 120°, so that it may be conveniently attached to a Pettenkoffer's absorption tube, the other end being connected, by means of a caoutchouc stopper and

* *Journal of Chemical Society*, March, 1879.

glass tubing, with an oxygen reservoir. This combustion tube is filled half way from the bent end with granulated cupric oxide, which may conveniently be held in position either by plugs of asbestos or by platinum wire gauze, or by a combination of both. The connection with the oxygen reservoir being then made, the greater part of the tube is heated to redness, with the ordinary precautions, and a stream of oxygen (which is first conducted through a long tube containing caustic potash) is passed over the glowing oxide of copper until the issuing gas ceases, after long bubbling, to cause any turbidity in the bright baryta water. As soon as this point is reached, the portion of the combustion tube preceding the layer of cupric oxide is allowed to cool somewhat, and the tube is now ready to be connected with the absorption apparatus. The clean absorption tube is carefully rinsed with water, and is clamped in front of the furnace in such a manner that its bulb end is somewhat higher than the end to be connected to the combustion tube. Both ends must be provided with convenient stoppers, consisting of short pieces of caoutchouc tubing closed with a small piece of glass rod. The stoppers being removed, air, which is first caused to pass through a tube containing caustic potash, is pumped through the tube for about two minutes, and it is then filled with baryta water as follows :—The baryta water (of strength 1·5 per cent.) is kept in a sufficiently large stock bottle, provided with a caoutchouc stopper, through which pass two bent glass tubes, the long one for syphoning, the shorter, to which a potash tube is attached, being connected with a small hand-bellows. In filling the absorption apparatus, the longer syphon tube is connected with it by means of flexible tubing, and the baryta water is forced over by gentle pressure of the bellows, the bulb end of the absorption apparatus being provided with a potash tube. As soon as the absorption apparatus is half filled, the flow of baryta water is arrested; the ends of the Pettenkoffer tube are immediately closed by its stoppers, and it is now ready for use. By these means the tube is filled with perfectly clear and bright baryta water. The absorption apparatus is now connected with the combustion tube, and the combustion proceeded with. The silver dish containing the water residue having been inserted just behind the copper oxide, it is burnt in a slow current of oxygen, and the carbon dioxide is absorbed and converted into baric carbonate in the absorption tube. In order to filter off and convert the baric carbonate, a funnel and filter are arranged to stand over a beaker containing a layer of caustic potash solution at the bottom, the whole being covered by a bell jar, which itself stands in a layer of caustic potash solution. The

mouth of the bell jar, which is immediately over the funnel, is closed by a thick caoutchouc cap with two narrow openings, one of which is provided with a caustic potash tube. (Soda lime apparently answers equally well.) The other, which is temporarily stoppered, contains a straight glass tube, placed immediately over the filter so that, after the whole arrangement has been left some time to itself, in order that all enclosed air may be free from CO_2, direct connection may be made with the Pettenkoffer tube by means of flexible tubing sufficiently long to admit of some slight freedom of action. Filtration may thus be carried on without danger of CO_2 being introduced from the atmosphere, the additional precaution being taken of compelling all air which passes through the Pettenkoffer tube during this process of filtration, to pass through a tube containing caustic potash attached to the tube itself. The washing of the precipitate in the tube and on the filter is effected almost entirely with boiling water, which has been previously saturated with carbonate of barium [solubility 1 in 15,000], but finally with a small quantity of boiling distilled water. After complete washing, the tube is disconnected, and the filter ultimately rinsed round, while still under the bell jar, by means of the long tube already mentioned, and which, when not clamped, may be moved freely in all directions. The bell jar is then removed, and the precipitate is rapidly washed together into the bottom of the filter.

The Pettenkoffer tube, which may contain minute particles of baric carbonate not removed by the washing, is rinsed twice with small quantities of dilute pure hydrochloric acid (about 1 in 50), and finally with distilled water: the rinsings are poured on to the filter on which the greater mass of baric carbonate is already collected. The filter is further washed with dilute hydrochloric acid, and finally with distilled water: and the whole of the solution of baric chloride so formed is carefully collected in a small beaker. The quantity of such solution need not exceed 50 cc. This solution of chloride of barium has next to be evaporated, which is best done in a platinum vessel on the water-bath. It is then transferred, when greatly decreased in bulk, to a much smaller platinum dish, weighing about 5 grms., and finally evaporated to dryness after the addition of a few drops of pure sulphuric acid. The dish and its contents have then to be ignited, the residue moistened with a drop of nitric acid and re-dried, and the whole re-ignited and weighed to conclude the operation. The amount of carbon present is obtained by dividing the weight of the baric sulphate by 19·4.

Nephalometric Method.—This ingenious method we also owe

to Dupré and Hake. The carbonic acid resulting from the combustion of an organic residue is passed into perfectly pure clear solution of basic lead acetate, and the turbidity produced is imitated by known weights of CO_2; in fact, the operation is a colour method conducted on the same principle as "Nesslerising," with this important difference, that no success will be obtained unless there are special precautions taken to prevent the contamination of the solutions by the breath and air, &c.

The Author's Method of Estimating Minute Quantities of Carbon.—The writer in 1881 made some very extended, and as yet unpublished, experiments on the estimation of organic carbon in the air, and the method was afterwards extended to all estimations of minute quantities of carbon dioxide, in which the balance from the small quantity present was likely to give less accurate results than measurement as a gas.

The method, briefly, consists of a suitable arrangement by which the carbon dioxide is absorbed in a solution of caustic potash, and ultimately evolved as gas. The arrangement for evolving the carbon dioxide absorbed as a gas is the same as that described at page 99, and is simplicity itself; in fact, the materials for the estimation merely consist of a flask with a caoutchouc cork, rod, and Bunsen's valve, an ordinary eudiometer and mercury trough, and lastly, a little test tube with sufficient acid to more than neutralise the potash. The solution in the flask is boiled briskly until all air is expelled, then the beak of the tube is put under the eudiometer, and the glass rod lifted up a little to allow the test tube to fall. A brisk effervescence takes place, and the whole of the gas as pure CO_2 is boiled out into the measuring tube. At first the author always proved its purity by again absorbing it with KHO, but as the result was always perfect absorption, this was abandoned. Of course, the gas is reduced to standard pressure and temperature.

That this method is applicable to the determination of the minute quantity of carbon in a water residue is obvious.*

Mineral Analysis of Water.—Ordinary drinking water holds dissolved but few saline matters, and when an analyst has determined chlorine, nitrates, sulphates, phosphates, and carbonates, and also lime and magnesia and alkalies, he will

*Other methods of determining organic elements have been proposed; one of the most recent is a proposition to estimate nitrogen as NH_3, by first treating the water with the zinc copper couple, expelling the ammonia thus produced by the decomposition of nitrates; boiling the solution to dryness with caustic soda in a copper flask, ultimately raising the heat to incineration; and condensing the products formed, and Nesslerising.—See "On a Method of Estimating Organic Nitrogen," by William Bettel—*Chemical News, Jan.* 27, 1882.

usually find, on adding the several amounts together, that he gets numbers very nearly equal to the solid saline residue. An excellent method of approximately estimating the various saline constituents of a water is to evaporate down to dryness a known quantity, then to treat the residue with a little hot water, which will dissolve all the soluble salts out, but leave insoluble carbonate of lime and silica. In the soluble portion, the soluble lime, the magnesia, and the alkalies are determined; the chlorides, sulphates, and nitrates, are estimated on the unconcentrated water by the processes already detailed. It is also always open to make the analysis in the old-fashioned way, that is, to evaporate down a large quantity of water, to separate the silica by treatment of the ash or residue with hydrochloric acid, and after separation of the silica to divide the solution into three or four quantities, in which sulphuric acid, lime, magnesia, &c., are determined by the ordinary methods.

IV. Biological Methods.

Fig. 49.

§ 320. A. *Microscopical Appearances.*—To make a microscopical examination of water, it is necessary to collect the sediment or deposit which falls to the bottom of the vessel in which the water stands. The most convenient way of doing this is to use the author's tube (fig. 49), which holds a little more than a litre. The little glass cell C is adjusted to the pipette-like end, the rod is removed, and after introduction of the water the tube is covered and set aside for twenty-four hours. At the end of that time any deposit will have collected in the glass cap. On now carefully inserting the rod-like stopper, the cap or cell can be removed with great ease, and its contents submitted to microscopical examination. With very pure waters merely a little sand or formless *débris* collects in the cap, and there is no life. If, however, in the first place eight or ten gallons are allowed to deposit in a capacious vessel, most of the water run off, and then the last litre rinsed into the tube, in nearly every case there may be a few life-forms and sufficient matter collected to give definite results. It need scarcely be said that an opinion must not be formed upon a microscopical examination without taking into account the amount of water from which the sediment has been collected, and a definite quantity should be generally agreed on by analysts. As for the present writer's practice—when a gallon of water throws down only mineral

matters and a little scanty unrecognisable *débris* without life-forms—although kept for at least twenty-four hours at a temperature of from 15° to 17°, and exposed to the daylight—he considers it, in a microscopical sense, pure. The contents of the little cap may be conveniently examined as follows:—By the aid of a pipette one or more drops are placed under the microscope without any preparation, others are divided upon several slides, and treated with (1.) dilute iodine solution, which will colour starch cells blue; (2.) aniline violet*—this is *par excellence* the staining fluid for bacteria; (3.) solution of carmine in glycerine and alcohol, which colours the nuclei of cells red. It will be advisable to work at first with a low power, so as to get a general idea of the nature of the larger and more opaque particles, and then afterwards investigate with the highest powers which the analyst possesses. In using low powers it is not well to place any covering glass over the drop, especially if a binocular be employed, for the convexity interferes in no way with the definition. The matters likely to be found in a water residue are—

1. *Lifeless Forms.*

1. *Mineral Matters*, especially sand, clay, and not unfrequently fine spicula of glass derived from the glass pipette, &c.

2. *Vegetable Matters.*—In shallow pools, in rivers, reservoirs, and, in fact, all open waters, the microscopist seldom fails to find vegetable *débris* in the shape of dotted ducts, spiral vessels, parenchymatous cells, bits of cuticle with the hair still adhering, the down of seeds, roots of duckweed, bits of chara, &c. It depends on the amount as to what conclusions are to be drawn; but this is certain, that a water showing these matters is not likely to be from a deep spring, but one over which the atmosphere more or less freely plays.

3. *Dead Animal Matters—(a.) Purely Animal*, such as hairs from domestic or wild animals, striped muscular tissue, the scales of moths, butterflies, or other lepidoptera, eggs of entozoa (which, of course, may, for aught we know, be living).

(b.) Human Débris.—Human hair, human epithelium.

(c.) Manufactured Matters.—Wool, silk, &c. All animal matters, whether derived from insect, human, or domestic animal life cannot be considered a favourable indication; and even the presence of cotton, silk, hemp, and the like, though

* The common aniline violet ink answers very well.

innocuous in themselves, yet afford evidence that the water is in such a position as to be liable to accidental contamination.

2. *Living Forms.*

The lower forms of vegetable and animal life spring from a common point, so that it is in certain cases impossible to definitely ascribe life-forms to either kingdom; nevertheless, it is convenient to divide provisionally the microscopic life-forms into (*a.*) *vegetable*, (*b.*) *animal.*

(*a.*) *Vegetable.*—The most common vegetable forms are confervæ, oscillatoria, volvocinæ, desmids, diatoms, and bacteria. To these may be added the green, or sometimes red, cells of palmellæ, and the moving reproductive spores of confervoids, charæ, &c. All of these, except the bacteria, diatoms, and certain spores, are distinguished by possessing cells holding "chlorophyll," and as such, always denote water which is exposed to daylight.


Fig. 50.

Desmids, beautiful microscopic algæ, consisting always of two symmetrical cells, are in colour remarkably green; one of the most common is a species of closterium (fig. 50). Desmids have been referred to by Dr. Macdonald as rather indicating a good water. It is true that desmids occurring by themselves, with no other indication of animal and vegetable life, could in no way be pronounced injurious. The fact, however, remains that, as a result of over ten years' experience in the almost daily analysis of water, the writer has never found desmids except in more or less surface supplies of water abounding with impurity. The diatoms, which are composed of a siliceous skeleton clothed by a sarcode substance, consist, like the desmids, of two exactly similar parts; they possess no chlorophyll, and probably belong to the animal kingdom. Fig. 51 is *Diatom vulgare*, very frequently found, and by itself certainly affording no indication of a bad water. In fact, diatoms generally are of little importance.


Fig. 51.

Bacteria.—This family of late years has excited a most extraordinary amount of attention and investigation, from the fact that certain forms of bacteria have been found the invariable associates of some virulent diseases, as, for example, malignant pustule. Bacteria are forms of extreme minuteness, the earliest appearance being that of points just visible with the highest powers of the microscope. Cohn defines them as chlorophyll-less cells of globular, oblong, or cylindrical form, multiplying exclusively through cell division, and vegetating either isolated or in families. Bacteria occur in water, (1.) as

clouds, well seen if a dead animal is allowed to putrefy in a salt water aquarium; (2.) as an iridescent film on the surface of water; (3.) as a pulverulent precipitate. The precipitate, where bacteria are plentiful, may form quite a layer, looking to the naked eye like fine white clay, but consisting of heaped up myriads of bacteria. Bacteria possess a motionless and an active condition; the movements are either those of rotation round their axis, or a passive bending and unbending of the curved forms. They are often in water very difficult to observe, because their index of refraction is so like that of water itself. The beautiful photographs which Dr. Koch has taken of various bacteria* show that they are not bounded by very definite lines, but that the dark body gradually blends into a gelatinous border or membrane. However difficult it is to observe bacteria when unstained, the aniline colours easily make them visible, and then it is at once seen how widely disseminated they are. Dr. Koch† recommends for photographic purposes a fluid containing bacteria to be treated thus: A drop of the fluid is taken out and placed on a glass slide, and covered with the usual thin covering glass. When the drop is dry or nearly so, it is remoistened with a solution of acetate of potash, 1:3, and then, if required, stained by an aniline brown; for mere detection of bacteria the methyl violet before alluded to is best, and one or two minutes immersion in a watery solution is sufficient. Cohn‡ divides bacteria thus—

I. Sphærobacteria (*Kugelbacterien*), minute jostling spheres. The cells are of an oval form, the dark body passes into the continuous membrane, and is not to be well separated from it; they occur in short chains or groups of 3, 4, and 8.§ To this division belong the ferment-producing (*zymogenous*) bacteria, as, for example, *Micrococcus ureæ*, always found wherever there is ammoniacal putrefaction. Another group is the *Chromogenous*, or colour-producing, as the *M. prodigiosus*, or blood-stain on bread, *M. violaceous*, discovered on slices of boiled potatoes, and many others. Another important subdivision is the "*Pathogenous*," or disease-producing, *e.g.*, *M. diphtherici*,‖ *M. vaccinniæ*, &c.

II. Microbacteria (*Stäbchenbacterien.*)—Minute short rods.

* "Untersuchungen über Bacterien; Verfahren zur Untersuchung, zum Conserviren u. Photographiren der Bacterien, von Dr. Koch. Beiträge zur Biologie der Pflanzen." Breslau, 1877. † *Op cit.*

‡ "Untersuchungen über Bacterien, von Dr. Ferdinand Cohn. Beiträge zur Biologie der Pflanzen." Breslau, 1872.

§ Pasteur calls single bacteria "*monads*," when in gelatinous masses "*mycoderma*." [Cohn's "Zooglea."]

‖ Oertel: Experimentelle Untersuchungen über Diphtherie. *Deutsche Archiv für Klinische Medizin.* Band vii., 1871.

This second class is separated from the first by their physiological activity, by their short cylindrical form, and the spontaneous movement of the cell. *B. termo* is *par excellence* the bacteria of putrefaction, and is the little organism to be found whenever and wherever any animal substance decays. The bacteria nearly always occur in pairs or dividing; they consist of very minute, little, short, cylindrical masses, either clear and transparent or blackish; there is a rather thick surrounding membrane. *B. lineola*, another member of this family, is larger, and is found in brooks and standing water; the cells are four times longer than broad, and have a strong refracting fatty nucleus.

III. DESMOBACTERIA (*Fadenbacterien*).—Thread or filament-like bacteria. The bacteria are in the shape of threads, some of them of great length. *B. anthracis* Cohn puts in this class.

IV. SPIROBACTERIA (*Schraubenbacterien*).—Spiral or screw-like filaments. This class includes vibrios and various species of spirillum.

The universal presence of bacteria, especially of the more common kinds, must render the microscopist cautious about conclusions, if he finds *a member or so in* water. If, however, water contains them in sufficient quantity to be a marked or unusual feature, such a water should be emphatically condemned.

(*b.*) *Animal Forms.*—Without taking into consideration various water insects which can be seen with the naked eye (*e.g.*, water fleas), but confining the attention solely to the microscopic forms of life, there is such an inexhaustible variety of the latter that it takes a special study to ascribe to each form its particular species; fortunately, this to the analyst is not necessary, and it may at once be laid down that if the deposit from a reasonable quantity of water (for example, a gallon) exhibits forms of infusorial life, the water cannot be pure. For although from all natural water, if a sufficient bulk be taken, it is possible to extract life-forms, yet all good drinking-water is devoid of such when moderate quantities are taken for the search. There are, however, certain animalcules (types of which are figured) that specially point to sewage contamination. This class have been called "saphrophiles."* They include most ciliated forms, such as paramecium, (fig. 52,6), glaucoma, as well as vorticella (fig. 52,1), amœba (fig. 52,8), and others. It will not be necessary to use any special colouring-agents to see infusoria, for they are quite sufficiently visible without any special reagent. M. A. Certes has, however, found out a colouring-matter which concentrates itself in certain parts of living infusoria, and may, therefore, be of some utility; this

* Under the saphrophiles belong all vegetable fungi, *e.g.*, leptothryx and infusoria thriving in filth.

reagent is quinoleine or cyanine, and it appears chiefly to colour the fatty parts of the protoplasm. He considers it a reagent for living fat.*

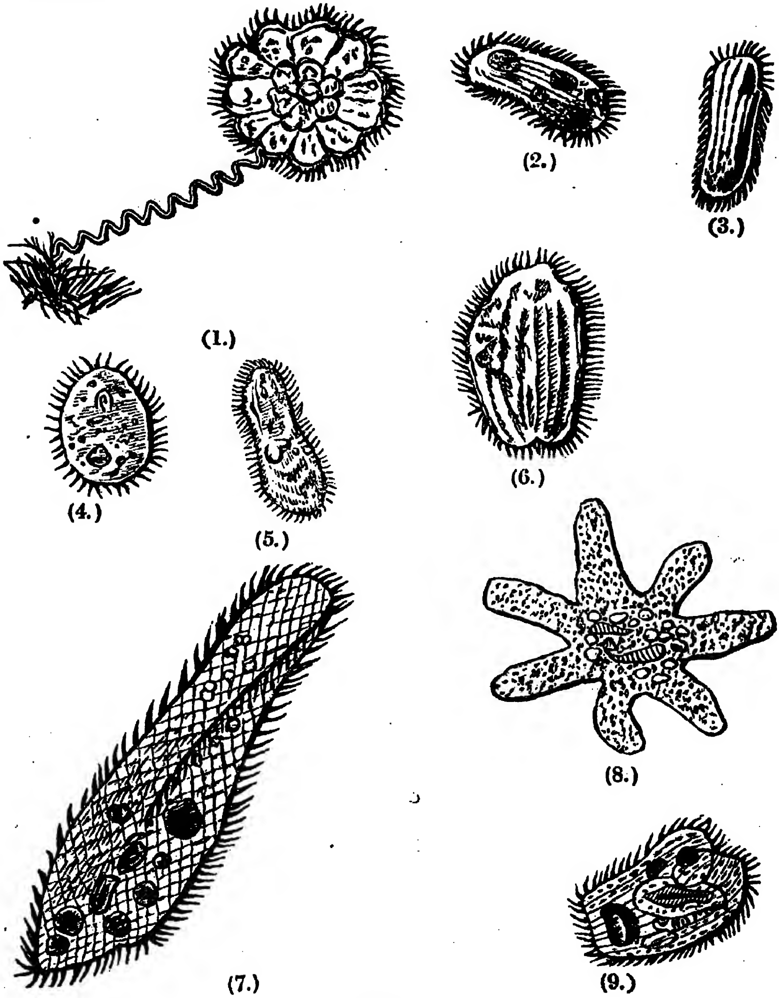

Fig 52.

1. Colony of Vorticella. 2. Oxytricha lingua. 3. Pellionella. 4. Glaucoma scintillans. 5. Glaucoma Gibba. 6. Paramæcium aurelia. 7. Paramæcium caudatum. 8. Amœba. 9. Chiloden.

* *Comptes Rendus*, xcii. 425.

B. *Cultivation of Germs, Fungi, &c.*—If a bottle of water carefully corked, and placed at a fermentation-temperature 20° to 24°, contain any putrescent matter, the water acquires a disagreeable smell, and when examined microscopically swarms with *B. termo* or other forms of low life. This simple test anyone can make for himself, and it is perhaps too much neglected. The best way to examine water thus fermented is to place a quantity of it in the special tube figured at p. 540; and, after adding a few drops of a 1 per cent. solution of osmic acid, to allow it to stand for some hours, then collect the sediment in the cap for microscopical examination, after the addition of methyl violet and other staining reagents. The osmic acid kills the life-forms; and they gradually sink to the bottom.

Heisch's Sugar Test.—Another fermentation method now much in use among analysts, is simply the addition of sugar to the water under examination, when, if the water contains the merest trace of sewage, a special fungus develops. The details of the test are as follows:—

A clean stoppered bottle, of any convenient size, is filled with the water, and a few grains of pure white sugar added. The bottle is now to be carefully stoppered, and placed at a fermentation temperature (26° to 27°). The growth of the fungus is rapid; at first small cells with a bright nucleus appear, changing within six hours to moniliform threads, and finally to cells mixed with mycelium. To trace the stages of the growth, it will be necessary to examine from time to time the liquid by the microscope; but the coarser changes may be watched with the naked eye: any water decidedly contaminated by sewage becomes quite turbid with the fungus in about twelve hours.

C. *Experiments on Animals and Human Beings.*—The biological examination of water embraces actual experiment on animals. Concentrated alcoholic, ethereal, or aqueous extracts of the water residue are injected by a fine syringe subcutaneously into small animals. From this important and direct method much may be hoped. A few experiments of the kind have been performed on the Continent; but in England, although foxes may be dug out to be eaten alive by hounds, and ratcatchers may poison rats by the gross, scientific men are unable, save under practically prohibitory restrictions, to advance biological science by the only satisfactory way, the use as a reagent for obscure poisons of life itself.

Experiments upon human beings are made necessarily daily, and on enormous masses of population. It is a kind of evidence that is most easily obtained, and nothing is more clearly proved than the fact, that a large population may drink a sewage-polluted

water with the utmost impunity, under certain conditions. A few years ago the author proved that a town in Somersetshire had drunk a water-supply from shallow wells which was nothing more nor less than dilute sewage; and yet the death-rates from fever, from dysentery, and all other diseases supposed (and rightly supposed) to be propagated by water, were remarkably low in comparison with places drinking a pure water. Here, then, was an experiment ready made on more than a thousand persons, and the negative results recorded for the best part of a century. It proved that under ordinary conditions the water was harmless, and yet what chemist could pass such? The colour, taste, and smell, as well as the organic carbon, nitrogen, and microscopical characters, all combined to show that the characters of the supply were of great impurity; on the other hand, water of very moderate impurity, as shown by ordinary chemical and microscopical investigation, has many times been as fatal as a solution of some subtle poison. These, as it were, unconscious experiments continuously proceeding in towns, in villages, and in solitary homes, demand the closest study; and such a study will in years to come make clear the apparent discrepancy often existing between chemical and biological analysis. Possibly the conclusion already shadowed forth is this:—water, however polluted by healthy human or animal sewage, nasty and abominable liquid as it may be, will produce no disease; water infected with the excretions from diseased natures will cause disease.

Since, however, at the present time we cannot differentiate between those excrementitious matters which cause disease, and those which do not cause disease, it is clearly safest to condemn as a supply a liquid which has been proved to be contaminated by a something, which, for aught we know, contains the seed of typhoid fever or of cholera.

D. *Experiments on Fish.*—It is in some instances extremely useful to study the effects of water upon living fish, especially in those cases in which there has been raised the question of whether a river or stream is polluted to such an extent as to destroy the fish in the stream. In experimenting as to whether a given water will support fish, it is essential to select healthy fish, fish suitable for the experiment, and to let the experiment go on for as long as possible. The best fish are the gold fish and the minnow, one or both. These can in towns be always purchased, and there is scarcely any country place in England in which minnows are not procurable. Besides, more is known as to the action of impurities on these fish, than on any other. The substances destructive to fish-life may be arranged in regard to their power of destruction in four classes:—

1. Sulphate of copper, the mineral acids; the sulphates of alum and iron, iodine, bromine, caustic potash or soda; the chlorides of tin, the heavy and light pitch oils, saturated solution of chloride of lime, and carbolic acid. These all destroy minnow life when contained in solution in so small a quantity as from 1 : 10,000, and some of them from 1 : 100,000.

2. The next in order of destroying-power are such as garancine, madder, sumach, catechu, acetic acid, citric acid, arsenious acid, gallic acid. These are all fatal when existing in the proportion of from 1 : 7000 of water, to from 1 : 3500.

3. The least destructive, but yet poisonous, agents are tartaric acid, salts of soda and potash, hydrate of lime, ammonia, bisulphide of carbon, sulphide of ammonium, sulphuretted hydrogen, foundry cake, furnace cinders, bleaching liquor.

4. Lastly come substances which are not directly poisonous, but induce a lowered vitality of the fish, so that it becomes attacked with a fungous growth.

The author found that a residue from gas-works, consisting of phenol and a mixture of hydrocarbons, though in less than 1 part per 10,000 of water, yet induced the growth of a fungus in the course of a few days on minnows, dace, roach, and rudd. The experiment was repeated many times, and always with the same result.

Organic matters, such as blood and urine, must be in a state of decomposition, and in such considerable quantities, that they deprive the water of oxygen before the fish are affected. Many oils appear to have no injurious effect on fish, as, for example, linseed and olive oil.

Symptoms.—In solutions that are not only poisonous, but also irritating to the surface of the body, the fish make frantic efforts to escape, and will often jump out of the water, rising to a considerable height. In solutions of poisonous substances generally, the symptoms to be looked for are: projection of the eyes, the frequent rising to the surface to breathe, loss of natural balance, disordered movements, loss of agility, especially the allowing of little masses of food to pass by unobserved, and, lastly, lying on the side at the top of the water.

§ 321. *Interpretation of Results.*—On many samples of water it takes some experience to give a really correct judgment, and it must ever be borne in mind that it is most unsafe to trust to an estimation of one or two constituents only. The report must be based upon a valuation of all the determinations, and a careful consideration of the general tendency of evidence. Great assistance will be derived in this by the aid of a scale by which a definite numerical value is assigned to the component parts of an

analysis. Such a scale has been invented by Mr. Wigner, and is now in provisional use by analysts.

§ 322. *Valuation of Water according to Mr. Wigner's Scale.*—In this scale, every constituent of the water as analysed by the Forchammer and ammonia processes has a definite value attached to it, and these values added together make the value of the water. It has been objected to the use of such a scale, that unless the history of the water is known, very erroneous conclusions may be drawn, and indeed it may be admitted that the scale is of far greater use in reports upon waters like the metropolitan, which are analysed from day to day throughout the year, than when operating on unknown samples. Nevertheless, there has always been a want of some definite expression of value, and as the scale is confessedly only a provisional one, the present writer thinks that it may be used generally with caution and discrimination.

The scale is as follows :—

Appearance in 2-ft. tube.		
Colour, blue,		0
,, pale yellow,		2
,, green,		2
,, dark yellow,		4
,, dark green,		4
Suspended matter to be added to valuation of appearance.		
For traces,		1
,, heavy traces,		2
,, turbidity,		4
Smell when heated to 100° F.		
Vegetable matter,		1
Strong peaty,		2
Offensive, of animal matter,		4
Chlorine in Chlorides,	·5 grs. per gal.	= 1
Phosphoric acid as Phosphates.		
Traces, = 2 h. traces = 4 v. h. traces		= 8
Nitrogen in Nitrates,	·100 gr. per gal.	= 1
Ammonia,	·005 gr. ,,	= 1
Albuminoid Ammonia,	·001 gr. ,,	= 1
Oxygen absorbed in 15 minutes at 80° Fahr.,	·002 gr. ,,	= 1
,, ,, 4 hours ,, ,,	·010 gr. ,,	= 1
Hardness before and after boiling added together,	5°	= 1
Total Solid Matter,	5 grs. per gal.	= 1
Heavy Metals,	S. traces	= 6
,, ,,	H. ,,	= 12
Microscopical results.		
Vegetable *débris* in small quantity,		4
,, ,, large ,,		8
Diatoms and Bacteria in small quantity,		6
,, ,, large ,,		12
Hairs, and animal *débris*, 10 to 20, according to the quantity observed.		

The following table gives the chemical results of the several monthly analyses of the Grand Junction water by the author, with the values according to the scale attached. The microscopical observations are omitted, because they were for the most part negative, and the chemical determinations being more easily followed will serve as a better example. The diagram is a graphical representation of the purity of the water according to the scale value. It will be admitted that on no other principle could the purity of a water be depicted by a single curve :—

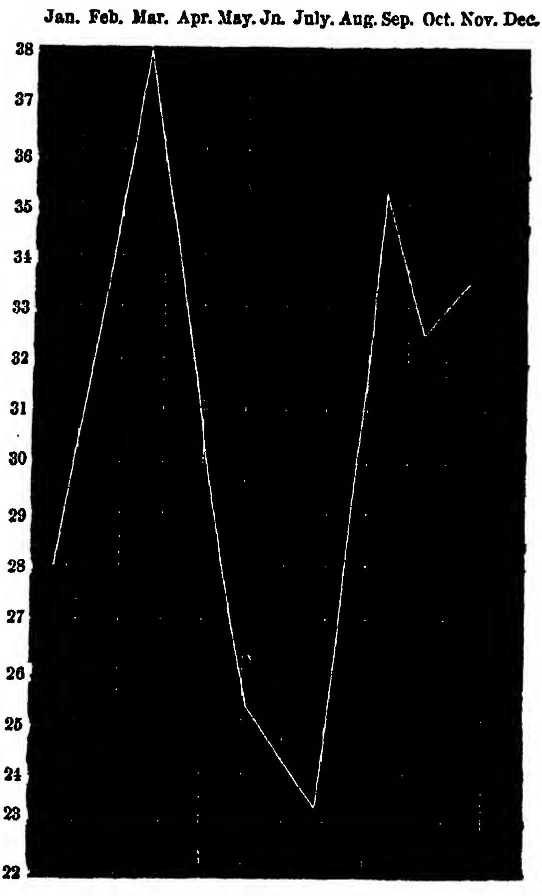

Fig. 53.

TABLE LIV.—GRAND JUNCTION WATER, 1881—ALL RESULTS ARE EXPRESSED IN GRAINS PER GALLON.

Description of Sample.	Appearance in Two-foot Tube.	Smell when heated to 100° F.	Chlorine.	Phosphoric Acid.	Nitrogen as Nitrates.	Ammonia.	Albuminoid Ammonia.	Oxygen Absorbed in		Hardness (Clark's Scale) in Degrees.		Total Solid Matter Dried at 220° F.	Valuation.
								2 mins. at 80° F.	4 hours at 80° F.	Before Boiling.	After Boiling.		
January, . .	Pale yellow.	0	1·12	Traces.	·1254	·0011	·0053	·0038	·0488	15·1	4·0	21·8	28·00
February, . .	Very pale yellow.	,,	1·20	,,	·1477	·0007	·0064	·0078	·0796	14·4	4·6	21·0	34·3
March, ...	,,	,,	1·26	,,	·1764	·0011	·0061	·0084	·1135	14·8	4·4	20·0	38·0
April, . . .	Pale yellow.	,,	0·96	S.trace	·1058	·0023	·0042	·0052	·0652	13·9	3·9	19·98	28·3
May, ...	,,	,,	1·06	,,	·1214	·0006	·0039	·0064	·0380	13·3	3·8	19·40	25·6
June, ...	,,	,,	1·10	,,	·1960	·0001	·0045	·0019	·0414	13·1	3·6	19·40	25·0
July, ...	,,	,,	1·04	,,	·0964	·0000	·0047	·0012	·0424	12·6	2·8	18·40	23·4
August, . . .	Very pale yellow.	,,	1·06	,,	·0922	·0002	·0059	·0012	·0631	12·3	3·0	17·80	26·5
September, . .	Pale yellow.	,,	1·12	,,	·2100	·0008	·0067	·0064	·0984	13·0	3·5	18·40	35·2
October, . . .	,,	,,	1·22	,,	·1610	·0010	·0069	·0031	·0840	14·1	3·9	20·00	32·5
November, . .	Pale straw colour.	,,	1·08	,,	·1680	·0000	·0066	·0257	·0964	15·4	4·2	21·50	33·6
December, . .	Pale yellow.	,,	1·24	,,	·1514	·0008	·0076	·0334	·0926	14·7	4·6	21·20	34·8

According to Mr. Wigner, a water which only values 15 is an extremely pure water. The limit of a first-class water would be about 40, of a second-class water, 65; anything beyond 65 would be a third-class water.

The scale at present gives no values for organic carbon or organic nitrogen; it will, therefore, be necessary to discuss briefly the limits within which organic carbon and organic nitrogen fall in good waters. With regard to these elements Dr. Frankland is the chemist who is most entitled to speak with authority. He considers that some importance should be attached, not only to the gross amount of carbon and nitrogen, but also to the relative proportion they bear to one another, and this especially with regard to surface waters. In deep springs the limit of organic carbon should be about ·1 in 100,000, the amount actually found ranging from ·02 to ·1 in 100,000 of water. In spring water the ratio of C : N varies from 2 : 1 to 6 : 1, with an average of about 2 : 1. Surface water derived from cultivated land, containing C : N below the proportion of 6 : 1, and having more than ·3 part of carbon in 100,000, with these data supported by other indications, should be condemned as unfit for dietetic purposes. In surface water, if carbon is to nitrogen as 3 : 1, the organic matter is of animal origin; if it be as high as 8 : 1, it is chiefly, if not exclusively, of vegetable origin. The content of organic elements in sewage, of course, varies according to its state of dilution; but it usually averages from four to five parts of carbon per 100,000, and from one to two parts of nitrogen per 100,000. Dr. Frankland divides waters into two sections, according to the results of a combustion.

Section I.—Upland Surface Water.

Class I.—Water of great organic purity, containing a portion of organic elements (organic carbon and organic nitrogen), not exceeding 0·2 part in 100,000 parts of water.

Class II.—Water of medium purity, containing from 0·2 to 0·4 part of organic elements in 100,000.

Class III.—Water of doubtful purity, containing from 0·4 to 0·6 part of organic elements in 100,000.

Class IV.—Impure water, containing more than 0·6 part of organic elements in 100,000.

Section II.—Water other than Upland Surface.

Class I.—Water of great organic purity, containing a proportion of organic elements not exceeding 0·1 part in 100,000.

Class II.—Water of medium purity, containing from 0·1 to 0·2 part of organic elements in 100,000.

Class III.—Water of doubtful purity, containing from 0·2 to 0·4 part of organic elements in 100,000.

Class IV.—Impure water, containing upwards of 0·4 part of organic elements in 100,000.

APPENDIX TO WATER ANALYSIS.

Standard Solutions and reagents &c., Alphabetically Arranged.

Parts by Weight: Liquids by Measure.

§ 323. *Ammonium Chloride.*—Ammonium chloride, ·3146 part; pure water, 1000 parts; dissolve. 1 cc. contains ·00001 grm. of ammonia, or 10 grains contain ·0001 grain.

Calcic Chloride Solution.—Iceland spar, or other pure form of calcic carbonate, ·2 part. Hydrochloric acid, *q. s.*; water, 1000 parts. The calcic carbonate is converted into chloride by evaporating to dryness with pure dilute hydrochloric acid, and the calcic chloride thus obtained is dissolved in water. The determination of hardness is usually made by English chemists in grains per gallon; then the following are the proportions—Calcium carbonate 8 grains; fully convert by dilute hydrochloric acid, evaporate to dryness, dissolve in water, and make up to one-tenth of a gallon; dilute ten times its volume, and the result is water of 8°.

Copper Sulphate.—Sulphate of copper 30 parts, pure water 1000 parts; dissolve.

Ferrous Chloride Solution.—A solution of pure ferrous sulphate is precipitated with sodic hydrate, and washed thoroughly with pure water, and then dissolved in the smallest possible quantity of pure hydrochloric acid.

Meta-phenylenediamine.—Meta-phenylenediamine 5 parts, water 1000 parts, sulphuric acid, *q. s.* The base is dissolved in the water, and then slightly supersaturated with sulphuric acid.

Meta-phosphoric Acid.—Meta-phosphoric acid 100 parts, made up to 1000 with distilled water; 10 parts should contain no appreciable amount of ammonia.

Molybdic Solution.—Molybdic acid, 1 part; solution of ammonia, specific gravity ·960, 4 parts; nitric acid, 1·20 specific gravity, 15 parts. The molybdic acid is dissolved in the ammonia, filtered, and poured with constant stirring into the nitric acid.

It should be kept in the dark, and freed by decantation from any precipitate which may form.

Nessler Solution.—35 parts of potassium iodide are dissolved in 100 parts of water; 17 parts of mercuric chloride are boiled in 300 parts of water, and then cooled. The mercuric solution is added to the potassium iodide, little by little, until a permanent precipitate is produced. The liquid is now made up to 1000 parts with a solution of sodic hydrate of 20 per cent. strength. Lastly, the reagent is made more sensitive by the final addition of a little more of the mercuric chloride solution, until a permanent precipitate begins to form. The solution is put on one side to deposit, and the clear liquid decanted for use. It is best to keep that intended for use in a small bottle, while the larger stock is carefully stoppered down.

Palladium Solution.—Palladium, ·1 part is dissolved in nitro-hydrochloric acid, and evaporated to dryness at 100°, 50 parts of hydrochloric are added, and 2000 of water, ultimately making the bulk up to 2,370 parts.

Potassium Iodide Solution.—(A.) Potassium iodide 1 part in 10 of water, for use in the oxygen or Forchammer process.

(B.) Potassium iodide 1, water 100,000, for use in the volumetrical estimation of iodine.

Potassium Monochromate.—Potassium monochromate 50 parts, dissolved in 1000 parts of distilled water. To ensure absence of chlorides it is recommended to add a little nitrate of silver until a permanent red precipitate forms, which is allowed to settle, and the clear solution used.

Potassium Permanganate.—(A.) *Alkaline*—Potassium permanganate 8 parts; potassium hydrate 200 parts; distilled water 1100 parts. The solution is boiled rapidly down to 1000 parts, and kept in properly stoppered bottles.

(B.) *Standard Volumetric Solution for Oxygen Process*—·395 part of potassic permanganate is dissolved in 1000 of water. Each cc. contains ·0001 gramme of available oxygen, and each one grain contains ·0001 grain.

Silver Nitrate, Standard Solution of.—4·7887 parts of silver nitrate are dissolved in pure water, and made up to 1000 parts. The solution may be standardised, if necessary, by the sodium chloride solution, 1 cc. = ·001 grm. chlorine; 10 grains = ·01 grain chlorine.

Soap, Standard Solution of.—150 parts of lead plaster are triturated in a mortar with 40 parts of dry potassic carbonate, and made into a cream with the addition of absolute alcohol; when dissolved, filter, and by the addition of water reduce the alcoholic strength to that of proof spirit. The solution of soap

is then reduced to the proper strength by proof spirit. If working in cc. and grms. it should be of such a strength that 14·25 cc. are required to form a permanent lather with 50 cc. of the calcic chloride solution; if working in grains, then it will be most convenient to make it of that strength that it just forms a permanent lather when 180 grain measures are shaken with 1000 grain measures of the standard calcic solution, equalling water of 8°.

Sodium Chloride Solution.—1·648 parts of pure sodium chloride are dissolved in water, and the solution made up to 1000 parts. Pure sodium chloride can be obtained by passing through a saturated solution of commercial sodic chloride hydrochloric acid gas; a precipitate of pure sodic chloride falls, which may be collected, and dried in the hot air oven at 260° to 300°. Each cc. contains ·001 grm. chlorine, or each grain contains ·001 grain chlorine.

Sodium Hydrate, Solution for Estimation of Nitrates.—56 parts of metallic sodium are dissolved little by little in 1000 parts of water.

Sodic Hyposulphite.—One part of crystallised sodium hyposulphite in 1000 parts of water.

Sodic Nitrite Solution.—·406 part of silver nitrite is dissolved in a little distilled water, and pure sodic chloride is added until no more argentic chloride is thrown down. Dilute with water to 1000 parts. Allow to settle. Then of the clear solution take 100 parts, and dilute to 1000; 1 cc. equals ·00001 grm. of N_2O_3; similarly each 10 grains equals ·0001 grain.

Starch Solution.—1 part of starch is rubbed up with 20 parts of boiling water. The liquid is filtered, boiled, and after being allowed to stand for twenty-four hours, the clear liquid is syphoned off.

TABLE LV., FOR HARDNESS IN GRAIN MEASURES (PAGE 327).

Degrees of Hardness.	Grain Measures.
Distilled Water = 0.	9
1.	29
2.	54
3.	77
4.	99
5.	120
6.	140
7.	160
8.	180
9.	200
10.	220
11.	240
12.	260
13.	280
14.	300
15.	320
16.	340

TABLE LVI.—OF HARDNESS IN PARTS PER 100,000—50 CC. OF WATER USED.

cc. of Soap Solution	$CaCO_3$ per 100,000.	cc. of Soap Solution	$CaCO_3$ per 100,000.	cc. of Soap Solution	$CaCO_3$ per 100,000.	cc. of Soap Solution	$CaCO_3$ per 100,000.
·7	·00	4·6	5·43	8·5	11·05	12·3	16·90
·8	·16	·7	·57	·6	·20	·4	17·06
·9	·32	·8	·71	·7	·35	·5	·22
1·0	·48	·9	·86	·8	·50	·6	·38
·1	·63	5·0	6·00	·9	·65	·7	·54
·2	·79	·1	·14	9·0	·80	·8	·70
·3	·95	·2	·29	·1	·95	·9	·86
·4	1·11	·3	·43	·2	12·11	13·0	18·02
·5	·27	·4	·57	·3	·26	·1	·17
·6	·43	·5	·71	·4	·41	·2	·33
·7	·56	·6	·86	·5	·56	·3	·49
·8	·69	·7	7·00	·6	·71	·4	·65
·9	·82	·8	·14	·7	·86	·5	·81
2·0	·95	·9	·29	·8	13·01	·6	·97
·1	2·08	6·0	·43	·9	·16	·7	19·13
·2	·21	·1	·57	10·0	·31	·8	·29
·3	·34	·2	·71	·1	·46	·9	·44
·4	·47	·3	·86	·2	·61	14·0	·60
·5	·60	·4	8·00	·3	·76	·1	·76
·6	·73	·5	·14	·4	·91	·2	·92
·7	·86	·6	·29	·5	14·06	·3	20·08
·8	·99	·7	·43	·6	·21	·4	·24
·9	3·12	·8	·57	·7	·37	·5	·40
3·0	·25	·9	·71	·8	·52	·6	·56
·1	·38	7·0	·86	·9	·68	·7	·71
·2	·51	·1	9·00	11·0	·84	·8	·87
·3	·64	·2	·14	·1	15·00	·9	21·03
·4	·77	·3	·29	·2	·16	15·0	·19
·5	·90	·4	·43	·3	·32	·1	·35
·6	4·03	·5	·57	·4	·48	·2	·51
·7	·16	·6	·71	·5	·63	·3	·68
·8	·29	·7	·86	·6	·79	·4	·85
·9	·43	·8	10·00	·7	·95	·5	22·02
4·0	·57	·9	·15	·8	16·11	·6	·18
·1	·71	8·0	·30	·9	·27	·7	·35
·2	·86	·1	·45	12·0	·43	·8	·52
·3	5·00	·2	·60	·1	·59	·9	·69
·4	·14	·3	·75	·2	·75	16·0	·86
·5	·29	·4	·90				

TABLE LVII.—Reduction of Cubic Centimetres of Nitrogen to Grammes.

$\log. \frac{0{\cdot}0012562}{(1+0{\cdot}00367\ )}760$ for each tenth of a degree from 0° to 30° C.

cc.	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
0	$\bar{6}$·21824	808	793	777	761	745	729	713	697	681
1	665	649	633	617	601	586	570	554	538	522
2	507	491	475	459	443	427	412	396	380	364
3	349	333	318	302	286	270	255	239	223	208
4	192	177	161	145	130	114	098	083	067	051
5	035	020	004	*989	*973	*957	*942	*926	*911	*895
6	$\bar{6}$·20879	864	848	833	817	801	786	770	755	739
7	723	708	692	676	661	645	629	614	598	583
8	567	552	536	521	505	490	474	459	443	428
9	413	397	382	366	351	335	320	304	289	274
10	259	244	228	213	198	182	167	151	136	121
11	106	090	075	060	045	029	014	*999	*984	*969
12	$\bar{6}$·19953	938	923	907	892	877	862	846	831	816
13	800	785	770	755	740	724	709	694	679	664
14	648	633	618	603	588	573	558	543	528	513
15	497	482	467	452	437	422	407	392	377	362
16	346	331	316	301	286	271	256	241	226	211
17	196	181	166	151	136	121	106	091	076	061
18	046	031	016	001	*986	*971	*956	*941	*926	*911
19	$\bar{6}$·18897	882	867	852	837	822	807	792	777	762
20	748	733	718	703	688	673	659	644	629	614
21	600	585	570	555	540	526	511	496	481	466
22	452	437	422	408	393	378	363	349	334	319
23	305	290	275	261	246	231	216	202	187	172
24	158	143	128	114	099	084	070	055	041	026
25	012	*997	*982	*968	*953	*938	*924	*909	*895	*880
26	$\bar{6}$·17866	851	837	822	808	793	779	764	750	735
27	721	706	692	677	663	648	634	619	605	590
28	576	561	547	532	518	503	489	475	460	446
29	432	417	403	388	374	360	345	331	316	302

ADDENDUM TO ARTICLE "BREAD," p. 171.

In a paper recently communicated to the Society of Public Analysts,* the author has shown that by treating flour or bread with a 5 per cent. solution of hydrochloric acid, acting in the cold, all soluble forms of alumina enter into solution, so that any alum present as alum, or any alumina present as phosphate of alumina, passes into the hydrochloric acid, and may be thus separated from silicates, and estimated by evaporating the acid to dryness, &c., as in treating a bread ash.

Great hopes were entertained that by this means accidental alumina in the form of silicates to the flour, and alumina as an adulterant might be distinguished; and, indeed, the earlier experiments of the author countenanced this view, but it was afterwards found that London clay and reddish clays generally contained phosphates of iron and alumina, while some second-class flour analysed by the author, and from which no trace of alum could be discovered by the chloroform process and by the gelatine logwood test, yet gave up to hydrochloric acid a considerable quantity of phosphate of alumina, the source of which was evidently a reddish clay which, by aid of chloroform, was easily separated.

A few words may be added as to the gelatine alum test: the most recent experience of the author tends more and more to confirm its delicacy and reliability. An important extension of the method consists in dissolving the alumed gelatine in a solution of purpurine or logwood, and submitting the solution to spectroscopic observation. For present purposes it will be necessary to have comparison solutions of alumed gelatine and unalumed gelatine, and compare the spectra side by side; but the author is making arrangements for their observation by photography. All recent workers in spectrum analysis have shown the great superiority of photography in spectroscopic work to that of the human eye. Not alone is there a faithful copy and permanent record of the spectra, but lines and bands are shown, otherwise quite invisible.

* Improved processes for the detection of alum in flour and bread. By A. Wynter Blyth, *Analyst*, February, 1882.

APPENDIX.

The Sale of Food and Drugs Act, 1875.

An Act to Repeal the Adulteration of Food Acts, and to Make Better Provision for the Sale of Food and Drugs in a Pure State. [38 & 39 Vict., ch. 63.]

Whereas it is desirable that the Acts now in force relating to the adulteration of food should be repealed, and that the law regarding the sale of food and drugs in a pure and genuine condition should be amended:

Be it therefore enacted by the Queen's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:

Repeal of 23 & 24 Vict. c. 84, & 31 & 32 Vict. c. 121 s 24, 33 & 34 Vict. c. 26 s 3, & 35 & 36 Vict. c. 74.

1. From the commencement of this Act the statutes of the twenty-third and twenty-fourth of Victoria, chapter eighty-four, of the thirty-first and thirty-second of Victoria, chapter one hundred and twenty-one, section twenty-four, of the thirty-third and thirty-fourth of Victoria, chapter twenty-six, section three, and of the thirty-fifth and thirty-sixth of Victoria, chapter seventy-four, shall be repealed, except in regard to any appointment made under them and not then determined, and in regard to any offence committed against them or any prosecution or other act commenced and not concluded or completed, and any payment of money then due in respect of any provision thereof.

Definitions.

2. The term "food" shall include every article used for food or drink by man, other than drugs or water:

The term "drug" shall include medicine for internal or external use:

The term "county" shall include every county, riding, and division, as well as every county of a city or town not being a borough:

The term "justices" shall include any police or stipendiary magistrate invested with the powers of a justice of the peace in England, and any divisional justices in Ireland.

Description of Offences.

Mixing, colouring, staining so as to injure health.

3. No person shall mix, colour, stain, or powder, or order or permit any other person to mix, colour, stain, or powder, any article of food with any ingredient or material so as to render the article injurious to health, with intent that the same may be sold in that state, and no person shall sell any such article so mixed, coloured, stained, or powdered, under a penalty in each case not exceeding fifty pounds for the first offence; every offence, after a conviction for a first offence, shall be a misdemeanor, for which the person, on conviction, shall be imprisoned for a period not exceeding six months with hard labour.

No drug to be coloured, &c., so as to injure its quality.

4. No person shall, except for the purpose of compounding as hereinafter described, mix, colour, stain, or powder, or order or permit any other person to mix, colour, stain, or powder, any drug with any ingredient or material so as to affect injuriously the quality or potency of such drug, with intent that the same may be sold in that state, and no person shall sell any such drug so mixed, coloured, stained, or powdered, under the same penalty in each case respectively as in the preceding section for a first and subsequent offence.

Guilty knowledge essential to the proof of the offence.

5. Provided that no person shall be liable to be convicted under either of the two last foregoing sections of this Act in respect of the sale of any article of food or of any drug, if he shows to the satisfaction of the justice or court before whom he is charged that he did not know of the article of food or drug sold by him being so mixed, coloured, stained, or powdered, as in either of those sections mentioned, and that he could not with reasonable diligence have obtained that knowledge.

No person to sell foods or drugs to the prejudice of purchaser.

6. No person shall sell to the prejudice of the purchaser any article of food or any drug which is not of the nature, substance, and quality of the article demanded by such purchaser, under a penalty not exceeding twenty pounds; provided that an offence shall not be deemed to be committed under this section in the following cases; that is to say,

Exceptions.

(1.) Where any matter or ingredient not injurious to health has been added to the food or drug because the same is required for the production or preparation thereof as an article of commerce, in a state fit for carriage or consumption, and not fraudulently to increase the bulk, weight, or measure of the food or drug, or conceal the inferior quality thereof:

(2.) Where the drug or food is a proprietary medicine, or is the subject of a patent in force, and is supplied in the state required by the specification of the patent:

(3.) Where the food or drug is compounded as in this Act mentioned:

(4.) Where the food or drug is unavoidably mixed with some extraneous matter in the process of collection or preparation.

Compound foods or drugs must be in accordance with the demands of purchase.

7. No person shall sell any compound article of food or compounded drug which is not composed of ingredients in accordance with the demand of the purchaser, under a penalty not exceeding twenty pounds.

A legible descriptive notice exonerates seller.

8. Provided that no person shall be guilty of any such offence as aforesaid in respect of the sale of an article of food or a drug mixed with any matter or ingredient not injurious to health, and not intended fraudulently to increase its bulk, weight, or measure, or conceal its inferior quality, if at the time of delivering such article or drug he shall supply to the person receiving the same a notice, by a label distinctly and legibly written or printed on or with the article or drug, to the effect that the same is mixed.

Abstraction of constituents of food.

9. No person shall, with the intent that the same may be sold in its altered state without notice, abstract from an article of food any part of it so as to affect injuriously its quality, substance, or nature, and no person shall sell any article so altered without making disclosure of the alteration, under a penalty in each case not exceeding twenty pounds.

Appointment and Duties of Analysts, and Proceedings to obtain the appointment of Analysis.

The local bodies by whom

10. In the city of London and the liberties thereof the Commissioners of Sewers of the City of London and the liberties thereof, and

in all other parts of the metropolis, the vestries and district boards acting in execution of the Act for the better local management of the metropolis, the court of quarter sessions of every county, and the town council of every burgh having a separate court of quarter sessions, or having under any general or local Act of Parliament or otherwise a separate police establishment, may, as soon as convenient after the passing of this Act, where no appointment has been hitherto made, and in all cases as and when vacancies in the office occur, or when required so to do by the Local Government Board, shall for their respective city, districts, counties, or boroughs, appoint one or more persons possessing competent knowledge, skill, and experience, as analysts of all articles of food and drugs sold within the said city, metropolitan districts, counties, or boroughs, and shall pay to such analysts such remuneration as shall be mutually agreed upon, and may remove him or them as they shall deem proper; but such appointments and removals shall at all times be subject to the approval of the Local Government Board, who may require satisfactory proof of competency to be supplied to them, and may give their approval absolutely or with modifications as to the period of the appointment and removal, or otherwise; Provided, that no person shall hereafter be appointed an analyst for any place under this section who shall be engaged directly or indirectly in any trade or business connected with the sale of food or drugs in such place.

analysts may be, or are to be, appointed in England.

In Scotland the like powers shall be conferred and the like duties shall be imposed upon the commissioners of supply at their ordinary meetings for counties, and the commissioners or boards of police, or where there are no such commissioners or boards, upon the town councils for burghs within their several jurisdictions; provided that one of Her Majesty's Principal Secretaries of State in Scotland shall be substituted for the Local Government Board of England.

Appointments in Scotland.

In Ireland the like powers and duties shall be conferred and imposed respectively upon the grand jury of every county and town council of every borough; provided that the Local Government Board of Ireland shall be substituted for the Local Government Board of England.

In Ireland.

11. The town council of any borough may agree that the analyst appointed by any neighbouring borough or for the county in which the borough is situated, shall act for their borough during such time as the said council shall think proper, and shall make due provision for the payment of his remuneration, and if such analyst shall consent, he shall during such time be the analyst for such borough for the purposes of the Act.

Town Councils may agree with analyst of neighbouring county or borough.

12. Any purchaser of any article of food or of a drug in any place being a district, county, city, or borough where there is any analyst appointed under this or any Act hereby repealed shall be entitled, on payment to such analyst of a sum not exceeding ten shillings and sixpence, or if there be no such analyst then acting for such place, to the analyst of another place, of such sum as may be agreed upon between such person and the analyst, to have such article analysed by such analyst, and to receive from him a certificate of the result of his analysis.

Any purchaser of foods or drugs is entitled, on payment of a fee, to have an analysis and certificate.

13. Any medical officer of health, inspector of nuisances, or inspector of weights and measures, or any inspector of a market, or any police constable under the direction and at the cost of the local authority appointing such officer, inspector, or constable, or charged with the execution of this Act, may procure any sample of food or drugs, and if he suspect the same to have been sold to him contrary to any provision of this Act, shall submit the same to be analysed by the analyst of the district or place for which he acts, or if there be no such analyst then acting for such place to the analyst of another place, and such analyst shall, upon receiving payment as is provided in

Medical officers of health, inspectors, and certain other officials may procure samples for analysis.

the last section, with all convenient speed analyse the same and give a certificate to such officer, wherein he shall specify the result of the analysis.

The person purchasing must notify his intention of having the article analysed by the public analyst, and divide it into three parts.

14. The person purchasing any article with the intention of submitting the same to analysis shall, after the purchase shall have been completed, forthwith notify to the seller or his agent selling the article his intention to have the same analysed by the public analyst, and shall offer to divide the article into three parts to be then and there separated, and each part to be marked and sealed or fastened up in such manner as its nature will permit, and shall, if required to do so, proceed accordingly, and shall deliver one of the parts to the seller or his agent.

He shall afterwards retain one of the said parts for future comparison, and submit the third part, if he deems it right to have the article analysed, to the analyst.

The seller not accepting, the analyst divides it into two parts.

15. If the seller or his agent do not accept the offer of the purchaser to divide the article purchased in his presence, the analyst receiving the article for analysis shall divide the same into two parts, and shall seal or fasten up one of those parts and shall cause it to be delivered, either upon receipt of the sample or when he supplies his certificate to the purchaser, who shall retain the same for production in case proceedings shall afterwards be taken in the matter.

Articles may be forwarded through the post.

16. If the analyst do not reside within two miles of the residence of the person requiring the article to be analysed, such article may be forwarded to the analyst through the post office as a registered letter, subject to any regulations which the Postmaster-General may make in reference to the carrying and delivery of such article, and the charge for the postage of such article shall be deemed one of the charges of this Act or of the prosecution, as the case may be.

Penalty for refusing to sell.

17. If any such officer, inspector, or constable, as above described, shall apply to purchase any article of food or any drug exposed to sale, or on sale by retail on any premises or in any shop or stores, and shall tender the price for the quantity which he shall require for the purpose of analysis, not being more than shall be reasonably requisite, and the person exposing the same for sale shall refuse to sell the same to such officer, inspector, or constable, such person shall be liable to a penalty not exceeding ten pounds.

Certificate.

18. The certificate of the analysis shall be in the form set forth in the schedule hereto, or the like effect.

Analysts must report quarterly.

19. Every analyst appointed under any Act hereby repealed or this Act shall report quarterly to the authority appointing him the number of articles analysed by him under this Act during the foregoing quarter, and shall specify the result of each analysis and the sum paid to him in respect thereof, and such report shall be presented at the next meeting of the authority appointing such analyst, and every such authority shall annually transmit to the Local Government Board, at such time and in such form as the Board shall direct, a certified copy of such quarterly report.

Proceedings against Offenders.

Proceedings after receipt of certificate.

20. When the analyst having analysed any article shall have given his certificate of the result, from which it may appear that an offence against some one of the provisions of this Act has been committed, the person causing the analysis to be made may take proceedings for the recovery of the penalty herein imposed for such offence, before any justices in petty sessions assembled having jurisdiction in the place where the article or drug sold was actually delivered to the purchaser, in a summary manner.

Recovery of penalties.

Every penalty imposed by this Act shall be recovered in England in the manner prescribed by the eleventh and twelfth of Victoria,

chapter forty-three. In Ireland such penalties and proceedings shall be recoverable, and may be taken with respect to the police district of Dublin metropolis, subject and according to the provisions of any Act regulating the powers and duties of justices of the peace for such district, or of the police of such district; and with respect to other parts of Ireland, before a justice or justices of the peace sitting in petty sessions, subject and according to the provisions of "The Petty Sessions (Ireland) Act, 1851," and any Act amending the same.

Every penalty herein imposed may be reduced or mitigated according to the judgment of the justices.

Production of certificate is evidence, but analyst must attend if required. The defendant or his wife may, if they choose, be examined

21. At the hearing of the information in such proceeding the production of the certificate of the analyst shall be sufficient evidence of the facts therein stated, unless the defendant shall require that the analyst shall be called as a witness, and the parts of the articles retained by the person who purchased the article shall be produced, and the defendant may, if he think fit, tender himself and his wife to be examined on his behalf, and he or she shall, if he so desire, be examined accordingly.

22. The justices before whom any complaint may be made, or the [illegible]

to Somerset House.

who shall thereupon direct the chemical officers of their department at Somerset House to make the analysis, and give a certificate to such justices of the result of the analysis; and the expense of such analysis shall be paid by the complainant or the defendant as the justices may by order direct.

Appeal to quarter sessions.

23. Any person who has been convicted of any offence punishable by any Act hereby repealed or by this Act by any justices may appeal in England to the next general or quarter sessions of the peace which shall be held for the city, county, town, or place wherein such conviction shall have been made, provided that such person enter into a recognisance within three days next after such conviction, with two sufficient sureties, conditioned to try such appeal, and to be forthcoming to abide the judgment and determination of the court at such general or quarter sessions, and to pay such costs as shall be by such court awarded; and the justices before whom such conviction shall be had are hereby empowered and required to take such recognisance; and the court at such general or quarter sessions are hereby required to hear and determine the matter of such appeal, and may award such costs to the party appealing or appealed against as they or he shall think proper.

Appeals in Ireland.

In Ireland any person who has been convicted of any offence punishable by this Act may appeal to the next court of quarter sessions to be held in the same division of the county where the conviction shall be made by any justice or justices in any petty sessions district, or to the recorder at his next sessions where the conviction shall be made by the divisional justices in the police district of Dublin metropolis, or to the recorder of any corporate or borough town when the conviction shall be made by any justice or justices in such corporate or borough town (unless when any such sessions shall commence within ten days from the date of any such conviction, in which case, if the appellant sees fit, the appeal may be made to the next succeeding sessions to be held for such division or town), and it shall be lawful for such court of quarter sessions or recorder (as the case may be) to decide such appeal, if made in such form and manner and with such notices as are required by the said Petty Sessions Acts respectively hereinbefore mentioned as to appeals against orders made by justices at petty sessions, and all the provisions of the said Petty Sessions Acts respectively as to making appeals and as to executing the orders made on appeal, or the original orders where the appeals

shall not be duly prosecuted, shall also apply to any appeal made under this Act.

Incumbent on defendant to prove that he comes within any exception with regard to mixed matters.

24. In any prosecution under this Act, where the fact of an article having been sold in a mixed state has been proved, if the defendant shall desire to rely upon any exception or provision contained in this Act, it shall be incumbent upon him to prove the same.

Written warranty a good defence.

25. If the defendant in any prosecution under this Act prove to the satisfaction of the justices or court that he had purchased the article in question as the same in nature, substance, and quality as that demanded of him by the prosecutor, and with a written warranty to that effect, that he had no reason to believe at the time when he sold it that the article was otherwise, and that he sold it in the same state as when he purchased it, he shall be discharged from the prosecution, but shall be liable to pay the costs incurred by the prosecutor, unless he shall have given due notice to him that he will rely on the above defence.

Penalties in England to go to the authority and be applied to expenses of Act. In Ireland in manner directed by Fines Act.

26. Every penalty imposed and recovered under this Act shall be paid in the case of a prosecution by any officer, inspector, or constable, of the authority who shall have appointed an analyst or agreed to the acting of an analyst within their district, to such officer, inspector, or constable, and shall be by him paid to the authority for whom he acts, and be applied towards the expenses of executing this Act, any Statute to the contrary notwithstanding; but in the case of any other prosecution the same shall be paid and applied in England according to the law regulating the application of penalties for offences punishable in a summary manner, and in Ireland in the manner directed by the Fines Act, Ireland, 1851, and the Acts amending the same.

Forged certificates.

27. Any person who shall forge, or shall utter, knowing it to be forged for the purposes of this Act, any certificate or any writing purporting to contain a warranty, shall be guilty of a misdemeanor and be punishable on conviction by imprisonment for a term of not exceeding two years with hard labour;

Every person who shall wilfully apply to an article of food, or a drug, in any proceedings under this Act, a certificate or warranty given in relation to any other article or drug, shall be guilty of an offence under this Act, and be liable to a penalty not exceeding twenty pounds;

Every person who shall give a false warranty in writing to any purchaser in respect of an article of food or a drug sold by him as principal or agent, shall be guilty of an offence under this Act, and be liable to a penalty not exceeding twenty pounds;

False labels.

And every person who shall wilfully give a label with any article sold by him which shall falsely describe the article sold, shall be guilty of an offence under this Act, and be liable to a penalty not exceeding twenty pounds.

Indictment.

28. Nothing in this Act contained shall affect the power of proceeding by indictment, or take away any other remedy against any offender under this Act, or in any way interfere with contracts and bargains between individuals, and the rights and remedies belonging thereto.

Breach of contract.

Provided that in any action brought by any person for a breach of contract on the sale of any article of food or of any drug, such person may recover alone or in addition to any other damages recoverable by him the amount of any penalty in which he may have been convicted under this Act, together with the costs paid by him upon such conviction and those incurred by him in and about his defence thereto, if he prove that the article or drug the subject of such conviction was sold to him as and for an article or drug of the same nature, substance, and quality as that which was demanded of him, and that he purchased it not knowing it to be otherwise, and

afterwards sold it in the same state in which he purchased it; the defendant in such action being nevertheless at liberty to prove that the conviction was wrongful, or that the amount of costs awarded or claimed was unreasonable.

Expenses of Executing the Act.

29. The expenses of executing this Act shall be borne, in the city of London and the liberties thereof, by the consolidated rates raised by the Commissioners of Sewers of the city of London and the liberties thereof, and in the rest of the metropolis by any rates or funds applicable to the purposes of the Act for the better local management of the metropolis, and otherwise as regards England, in counties by the county rate, and in boroughs by the borough fund or rate; Expenses in England.

And as regards Ireland, in counties by the grand jury cess, and in boroughs by the borough fund or rate; all such expenses payable in any county out of grand jury cess shall be paid by the treasurer of such county; and In Ireland.

The grand jury of any such county shall, at any assizes at which it is proved that any such expenses have been incurred or paid without previous application to presentment sessions, present to be raised off and paid by such county the moneys required to defray the same.

Special Provision as to Tea.

30. From and after the first day of January one thousand eight hundred and seventy-six all tea imported as merchandise into and landed at any port in Great Britain or Ireland shall be subject to examination by persons to be appointed by the Commissioners of Customs, subject to the approval of the Treasury, for the inspection and analysis thereof, for which purpose samples may, when deemed necessary by such inspectors, be taken, and with all convenient speed be examined by the analysts to be so appointed; and if upon such analysis the same shall be found to be mixed with other substances or exhausted tea, the same shall not be delivered unless with the sanction of the said commissioners, and on such terms and conditions as they shall see fit to direct, either for home consumption or for use as ships' stores or for exportation; but if on such inspection and analysis it shall appear that such tea is in the opinion of the analyst unfit for human food, the same shall be forfeited and destroyed or otherwise disposed of in such manner as the said commissioners may direct. Special provisions as to tea.

31. Tea to which the term "exhausted" is applied in this Act shall mean and include any tea which has been deprived of its proper quality, strength, or virtue by steeping, infusion, decoction, or other means.

32. For the purposes of this Act every liberty of a cinque port not comprised within the jurisdiction of a borough shall be part of the county in which it is situated, and subject to the jurisdiction of the justices of such county. Cinque ports.

33. In the application of this Act to Scotland the following provisions shall have effect: Special applications to

1. The term "misdemeanor" shall mean "a crime or offence:"
2. The term "defendant" shall mean "defender," and include "respondent:"
3. The term "information" shall include "complaint:"
4. This Act shall be read and construed as if for the term

"justices," wherever it occurs therein, the term "sheriff" were substituted:

5. The term "sheriff" shall include "sheriff-substitute:"

Definitions of borough.

6. The term "borough" shall mean any royal burgh and any burgh returning or contributing to return a member to Parliament:

Expenses.

7. The expenses of executing this Act shall be borne in Scotland, in counties, by the county general assessment, and in burghs, by the police assessment:

Local Government Board.

8. This Act shall be read and construed as if for the expression "the Local Government Board," wherever it occurs therein, the expression "one of Her Majesty's Principal Secretaries of State" were substituted:

Penalties.

9. All penalties provided by this Act to be recovered in a summary manner shall be recovered before the sheriff of the county in the sheriff court, or at the option of the person seeking to recover the same in the police court, in any place where a sheriff officiates as a police magistrate under the provisions of "The Summary Procedure Act, 1864," or of the Police Act in force for the time in any place in which a sheriff officiates as aforesaid, and all the jurisdiction, powers, and authorities necessary for this purposes are hereby conferred on sheriffs:

Every such penalty may be recovered at the instance of the procurator-fiscal of the jurisdiction, or of the person who caused the analyses to be made from which it appeared that an offence had been committed against some one of the provisions of this Act.

Every penalty imposed and recovered under this Act shall be paid to the clerk of court, and by him shall be accounted for and paid to the treasurer of the county general assessment, or the police assessment of the burgh, as the sheriff shall direct.

10. Every penalty imposed by this Act may be reduced or mitigated according to the judgment of the sheriff:

11. It shall be competent to any person aggrieved by any conviction by a sheriff in any summary proceeding under this Act to appeal against the same to the next circuit court, or where there are no circuit courts to the High Court of Justiciary at Edinburgh, in the manner prescribed by such of the provisions of the Act of the twentieth year of the reign of King George the Second, chapter forty-three, and any Acts amending the same, as relate to appeals in matters criminal, and by and under the rules, limitations, conditions, and restrictions contained in the said provisions.

Special applications to Ireland.

34. In the application of this Act to Ireland,—

Definitions.

Borough.

The term "borough" shall mean any borough subject to the Act of the session of the third and fourth years of the reign of Her present Majesty, chapter one hundred and eight, intituled "An Act for the Regulation of Municipal Corporations in Ireland."

County.

The term "county" shall include a county of a city and a county of a town not being a borough.

Assizes.

The term "assizes" shall, with respect to the county of Dublin, mean "presenting term."

Treasurer.

The term "treasurer of the county" shall include any person or persons or bank in any county performing duties analogous to those of the treasurer of the county in counties, and, with respect to the county of Dublin, it shall mean the finance committee:

Police constable.

The term "police constable," shall mean, with respect to the police district of Dublin metropolis, constable of the Dublin Metropolitan Police, and with respect to any other part of Ireland, constable of the Royal Irish Constabulary:

Commencement of Act

35. This Act shall commence on the first day of October one thousand eight hundred and seventy-five.

36. This Act may be cited as "The Sale of Food and Drugs Act, 1875." Title.

SCHEDULE.

Schedule.

FORM OF CERTIFICATE.

To*

I, the undersigned, public analyst for the , do hereby certify that I received on the day of , 18 , from† , a sample of for analysis (which then weighed‡), and have analysed the same, and declare the result of my analysis to be as follows:— Certificate.

I am of opinion that the same is a sample of genuine

or,

I am of opinion that the said sample contained the parts as under, or the percentages of foreign ingredients as under.

Observations.§

As witness my hand this day of

A. B.

at

* Here insert the name of the person submitting the article for analysis.

† Here insert the name of the person delivering the sample.

‡ When the article cannot be conveniently weighed, this passage may be erased, or the blank may be left unfilled.

§ Here the analyst may insert at his discretion his opinion as to whether the mixture (if any) was for the purpose of rendering the article portable or palatable, or of preserving it, or of improving the appearance, or was unavoidable, and may state whether in excess of what is ordinary, or otherwise, and whether the ingredients or materials mixed are or are not injurious to health.

In the case of a certificate regarding milk, butter, or any article liable to decomposition, the analyst shall specially report whether any change had taken place in the constitution of the article that would interfere with the analysis.

Sale of Food and Drugs Act Amendment Act, 1879, [42 & 43 Vict. c. 30.]

38 & 39 Vict. c. 63.

Whereas conflicting decisions have been given in England and in Scotland in regard to the meaning and effect of section six of the Sale of Food and Drugs Act, 1875, in this Act referred to as the principal Act, and it is expedient, in this respect and otherwise, to amend the said Act: Be it enacted by the Queen's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:

Short title.

1. This Act may be cited for all purposes as the Sale of Food and Drugs Act Amendment Act, 1879.

In sale of adulterated articles, no defence to allege purchase for analysis.

2. In any prosecution under the provisions of the principal Act for selling to the prejudice of the purchaser any article of food or any drug which is not of the nature, substance, and quality of the article demanded by such purchaser, it shall be no defence to any such prosecution to allege that the purchaser, having bought only for analysis, was not prejudiced by such sale. Neither shall it be a good defence to prove that the article of food or drug in question, though defective in nature or in substance or in quality, was not defective in all three respects.

Officer, inspector, or constable may obtain a sample of milk at the place of delivery to submit to analyst.

3. Any medical officer of health, inspector of nuisances, or inspector of weights and measures, or any inspector of a market, or any police constable under the direction and at the cost of the local authority appointing such officer, inspector, or constable, or charged with the execution of this Act, may procure at the place of delivery any sample of any milk in course of delivery to the purchaser or consignee in pursuance of any contract for the sale to such purchaser or consignee of such milk; and such officer, inspector, or constable, if he suspect the same to have been sold contrary to any of the provisions of the principal Act, shall submit the same to be analysed, and the same shall be analysed, and proceedings shall be taken, and penalties on conviction be enforced in like manner in all respects as if such officer, inspector, or constable had purchased the same from the seller or consignor under section thirteen of the principal Act.

Penalty for refusal to give milk for analysis.

4. The seller or consignor or any person or persons entrusted by him for the time being with the charge of such milk, if he shall refuse to allow such officer, inspector, or constable to take the quantity which such officer, inspector, or constable shall require for the purpose of analysis, shall be liable to a penalty not exceeding ten pounds.

Extension of Act as to sale in streets, &c.

5. Any street or open place of public resort shall be held to come within the meaning of section seventeen of the principal Act.

Reduction allowed to the extent of 25 degrees under proof for brandy, whisky, or rum, and 35 degrees for gin.

6. In determining whether an offence has been committed under section six of the said Act by selling, to the prejudice of the purchaser, spirits not adulterated otherwise than by the admixture of water, it shall be a good defence to prove that such admixture has not reduced the spirit more than twenty-five degrees under proof for brandy, whisky, or rum, or thirty-five degrees under proof for gin.

Extension of meaning of "county."

7. Every liberty having a separate court of quarter sessions, except a liberty of a cinque port, shall be deemed to be a county within the meaning of the said Act.

Quarter session boroughs not to contribute to county analyst.

8. The town council of any borough having a separate court of quarter sessions shall be exempt from contributing towards the expenses incurred in the execution of the principal Act in respect of the county within which such borough is situate, and the treasurer of the county shall exclude the expenses so incurred from the account required by section one hundred and seventeen of the Municipal Corporation Act, 1835, to be sent by him to such town council.

5 & 6 W. 4. c. 76.

9. The town council of any borough having under any general or local Act of Parliament, or otherwise, a separate police establishment, and being liable to be assessed to the county rate of the county within which the borough is situate, shall be paid by the justices of such county the proportionate amount contributed towards the expenses incurred by the county in the execution of the principal Act by the several parishes and parts of parishes within such borough in respect of the rateable value of the property assessable therein, as ascertained by the valuation lists for the time being in force. Provision for boroughs with separate police.

10. In all prosecutions under the principal Act, and notwithstanding the provisions of section twenty of the said Act, the summons to appear before the magistrates shall be served upon the person charged with violating the provisions of the said Act within a reasonable time, and in the case of a perishable article not exceeding twenty-eight days from the time of the purchase from such person for test purposes of the food or drug, for the sale of which in contravention to the terms of the principal Act the seller is rendered liable to prosecution, and particulars of the offence or offences against the said Act of which the seller is accused, and also the name of the prosecutor, shall be stated on the summons, and the summons shall not be made returnable in a less time than seven days from the day it is served upon the person summoned. Special provision as to time for proceedings.

New York Adulteration Act, 1881.

An Act to Prevent the Adulteration of Food or Drugs, 1881.

The People of the State of New York, represented in Senate and Assembly, do enact as follows:—

Section 1.—No person shall, within this State, manufacture, have, offer for sale, or sell any article of food or drugs which is adulterated within the meaning of this Act, and any person violating this provision shall be deemed guilty of a misdemeanor, and upon conviction thereof, shall be punished by fine not exceeding fifty dollars for the first offence, and not exceeding one hundred dollars for each subsequent offence.

Section 2.—The term "food," as used in this Act, shall include every article used for food or drink by man. The term "drug," as used in this Act, shall include all medicines for internal and external use.

Section 3.—An article shall be deemed to be adulterated within the meaning of this Act.

(*a.*)—In the case of drugs—

1. If, when sold under or by a name recognised in the United States Pharmacopœia, it differs from the standard of strength, quality, or purity laid down therein.

2. If, when sold under or by a name not recognised in the United States Pharmacopœia, but which is found in some other Pharmacopœia or other standard work on Materia Medica, it differs materially from the standard of strength, quality, or purity laid down in such work.

3. If its strength or purity fall below the professed standard under which it is sold.

(*b.*) In the case of food or drink—

1. If any substance or substances has or have been mixed with it so as to reduce or lower or injuriously affect its quality or strength.

2. If any inferior or cheaper substance or substances have been substituted wholly or in part for the article.

3. If any valuable constituent of the article has been wholly or in part abstracted.

4. If it be an imitation of, or be sold under the name of, another article.

5. If it consists wholly or in part of a diseased or decomposed, or putrid or rotten, animal or vegetable substance, whether manufactured or not, or, in the case of milk, if it is the produce of a diseased animal.

6. If it be coloured, or coated, or polished, or powdered, whereby damage is concealed, or it is made to appear better than it really is, or of greater value.

7. If it contain any added poisonous ingredient, or any ingredient which may render such an article injurious to the health of a person consuming it. Provided, that the State board of health may, with the approval of the governor, from time to time declare certain articles or preparations to be exempt from the provisions of this Act: And provided further, that the provisions of this Act shall not apply to mixtures or compounds recognised as ordinary articles of food, provided that the same are not injurious to health and that the articles are distinctly labelled as a mixture, stating the components of the mixture.

Section 4.—It shall be the duty of the State board of health to prepare and publish from time to time, lists of the articles, mixtures or compounds declared to be exempt from the provisions of this Act in accordance with the preceding section. The State board of health shall also from time to time fix the limits of variability permissible in any article of food or drug, or compound, the standard of which is not established by any national Pharmacopœia.

Section 5.—The State board of health shall take cognisance of the interests of the public health as it relates to the sale of food and drugs, and the adulteration of the same, and make all necessary investigations and inquiries relating thereto. It shall also have the supervision of the appointment of Public Analysts and Chemists, and upon its recommendation, whenever it shall deem such officers incompetent, the appointment of any and every such officer shall be revoked and be held to be void and of no effect. Within thirty days after the passage of this Act, the State board of health shall meet and adopt such measures as may seem necessary to facilitate the enforcement of this Act, and prepare rules and regulations with regard to the proper methods of collecting and examining articles of food or drugs, and for the appointment of the necessary inspectors and analysts; and the State board of health shall be authorised to expend, in addition to all sums already appropriated for said board, an amount not exceeding ten thousand dollars for the purpose of carrying out the provisions of this Act. And the sum of ten thousand dollars is hereby appropriated out of the moneys in the treasury, not otherwise appropriated, for the purposes in this section provided.

Section 6.—Every person selling or offering or exposing any article of food or drugs for sale, or delivering any article to purchasers, shall be bound to serve or supply any Public Analyst or other agent of the State or local board of health appointed under this Act, who shall apply to him for that purpose, and on his tendering the value of the same, with a sample sufficient for the purpose of analysis of any article which is included in this Act, and which is in the possession of the person selling, under a penalty not exceeding fifty dollars for a first offence, and one hundred dollars for a second and subsequent offences.

Section 7.—Any violation of the provisions of this Act shall be treated and punished as a misdemeanor; and whoever shall impede, obstruct, hinder, or otherwise prevent any Analyst, Inspector, or

prosecuting officer in the performance of his duty shall be guilty of a misdemeanor, and shall be liable to indictment and punishment therefor.

Section 8.—Any Acts or parts of Acts inconsistent with the provisions of this Act are hereby repealed.

Section 9.—All the regulations and declarations of the State board of health made under this Act, from time to time, and promulgated, shall be printed in the statutes at large.

Section 10.—This Act shall take effect at the expiration of ninety days after it shall become law.

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